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The Coordination and Activation of Organic Isothiocyanates and Related Molecules in the Presence of Two Metal Centers

by

© John Andrew Edwin Gibson

A THESIS

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Date.....5/12/1983.....

ABSTRACT

The reactions of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (DPM = $Ph_2PCH_2PPh_2$) with the isothiocyanate molecules RC(O)NCS (R = EtO, Ph) yield the complexes $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)R)(DPM)_2]$, in which the metals are bridged by the carbonyl ligand and the isothiocyanate molecule with no accompanying metal-metal bond. The carbonyl group of the isothiocyanate ligand is also coordinated to one of the Rh centers. In solution each of these species is in equilibrium with an isomeric form having a terminal carbonyl ligand and a Rh-Rh bond. $[Rh_2I_2(CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ can be prepared from $[Rh_2I_2(\mu\text{-}CO)(DPM)_2]$ but only exists as the Rh-Rh bonded isomer. $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ reacts with one equivalent of CO to give $[Rh_2Cl_2(CO)(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ and reacts with additional CO to give $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CPM)_2][Cl]$. The benzoylisothiocyanate analogue also reacts with CO but only the above tricarbonyl species, resulting from isothiocyanate displacement, is observed. Both isothiocyanate adducts react with MeNC to give $[Rh_2Cl_2(CNMe)(\mu\text{-}CO)(SCNC(O)R)(DPM)_2]$. The reactions of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ with PhNCS and MeNCS yield a variety of products of which the only species identified are $[Rh_2Cl_2(CO)(CNR)(DPM)_2]$ (R = Ph, Me). $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ reacts with isothiocyanates and CS_2 to

yield $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(R)C(O)OEt)(DPM)_2]$ (R = Me, Ph, C(O)OEt, C(O)Ph) and $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)SC(O)OEt)(DPM)_2]$, respectively, and an X-ray structure determination of one product (R = Ph) indicates that condensation of the isothiocyanate molecules has occurred with C-N bond formation, accompanied by migration of the C(O)OEt moiety to the nitrogen atom of the PhNCS group. The unusual tridentate ligand which results can be viewed as a new isothiocyanate group, RNCS, with R = C(S)N(Ph)C(O)OEt. This group bridges the metals, bound to one via the sulfur and to the other via the carbon of the isothiocyanate group, and is additionally coordinated to one metal center by the thiocarbonyl moiety.

Oxidative addition of $SC(Cl)NMe_2$ to $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ yields $[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$ or, in the presence of BF_4^-, $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$. An X-ray structure determination of the latter compound shows that the $SCNMe_2$ moiety is bound in an η^2 fashion to one metal center. The BF_4^- salt reacts with Me_3NO, resulting in carbonyl loss and the formation of $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ in which the $SCNMe_2$ moiety bridges the metals. This reaction is readily reversed by addition of CO; reaction with CNMe produces $[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$. Reduction of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ with BH_4^- yields the very

air sensitive compounds $[Rh_2(CO)(Solvent)(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (Solvent = THF or acetonitrile), which in turn react with CO to form the more stable $[Rh_2(CO)_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$.

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ABBREVIATIONS

av.	average
Cy	cyclohexyl
diars	o-phenylenebis(dimethylarsine)
DPM	bis(diphenylphosphino)methane
Et	ethyl
h	hour
Me	methyl
NMR	nuclear magnetic resonance
ppm	parts per million
Ph	phenyl
THF	tetrahydrofuran

CHAPTER ONE

INTRODUCTION

Inorganic chemistry was, for many years, concerned mainly with the study of compounds containing a single metal centre.[1] However, recently there has been increasing interest paid to species containing more than one metal centre, in which the metals are held together by bridging ligands, metal-metal bonds, or both.[1-12] Much of the initial interest in these polynuclear compounds was devoted to the elucidation of their structural, bonding and electronic properties.[2-7] There is now, however, a growing recognition that the reactivity patterns associated with polynuclear compounds will provide a rich and fruitful area of research.[8-12]

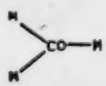
Two of the most important aspects of polynuclear metal chemistry concern the coordination and the reactivity of ligands which are simultaneously bound to more than one metal centre.[13-14] In both cases, chemistry without precedent in mononuclear systems can be observed.

In complexes containing a single metal centre, ligands are generally constrained to one of a small number of bonding modes. However, in polynuclear species ligands

which are capable of interacting simultaneously with more than one metal have a much wider variety of bonding options available to them. This is possibly best illustrated by the coordination modes available to small molecules such as carbon monoxide in the presence of more than one metal center.[15-16] In mononuclear species, CO binds to metals exclusively in a linear fashion through the carbon atom, but in polynuclear species, many more coordination modes are observed, some of which are listed in Table 1. The effects that the differing coordination modes have on the electronic distribution within the ligand are reflected by the carbonyl stretching frequencies observed for the various modes (see Table 1). It is not unreasonable to expect that the various electron distributions within coordinated ligands should give rise to different reactivities, therefore the cooperative action of two or more metals on a substrate molecule might be expected to result in reactivity patterns not observed in mononuclear complexes.

The possible effects of two or more metal centers, which are in close proximity to one another, on the chemistry observed is not limited to the cooperative activation of substrate molecules. One can envision the possibility of coordination of substrates, one at each of two adjacent metal centers, allowing the movement of these substrates together for some specific interaction,[27] for

Table 1. Observed Coordination Modes of the Carbonyl Ligand.

Mode		Example	ν(CO) cm^{-1}	Ref
terminal	M—CO	trans-[RhCl(CO)$(PPh_3)_2$]	1980	17
symmetric-μ_2		[$Fe_2(CO)_6$(μ-CO)(DPM)]	1770	18
asymmetric-μ_2		[Rh(CO)(μ-CO)$(PPh_3)_2]_2$	1740	19
semibridging-μ_2		[$Fe_2(CO)_6$(μ-CO)(PhCCPh)]	1840	20
Linear-μ_2		[$Mn_2(CO)_4$(μ-CO)$(DPM)_2$]	1645	21
ketonic-μ_2		[Rh_2Cl_2(μ-CO)-(μ-CF_3CCCF_3)$(DPM)_2$]	1700	22
triply-bridging		$[Co_6(CO)_{14}]^{4-}$	1660	23
quadruply-bridging		$[Fe_4H(CO)_{13}]^-$	1723	24
isocarbonyl	M—CO—M	[$(Cp^*)_2$(THF)YbOCCo$(CO)_3$]	1761	25
bridging isocarbonyl		[CpFe(CO)(μ-COAlEt_3)$]_2$	1682	26

example, a ligand coupling reaction.[28] Furthermore, polynuclear species also have the capability of redistributing their ligands by migration from one centre to another thereby creating a vacant coordination site on a particular metal centre.[29,30] For mononuclear species, ligand dissociation is required for generation of a vacant coordination site, a process which should be more difficult than the ligand rearrangement of the polynuclear species.

The cooperative action of metals on, and the consequent potentially novel reactivity of, ligands in polynuclear complexes has led to a great deal of activity investigating the use of such species as catalysts for organic and inorganic reactions.[31] In particular, it is hoped that the new reaction pathways open to ligands will lead to the development of processes which are either improvements on known mononuclear catalytic reactions or which provide new, useful transformations of substrates into desirable products that are not possible in mononuclear systems. A number of reactions have, in fact, been found to be catalyzed by polynculear species. Examples include the isomerization,[32,33] hydrogenation[33] and hydroformylation[34] of olefins, Fisher-Tropsch chemistry,[35] and the Water Gas Shift reaction.[36,37]

Polynuclear complexes have relevance in two other fields of catalysis research. Studies have been undertaken

probing the relationship between metal clusters (polynuclar metal compounds held together by metal-metal bonds) and metal surfaces,[38] in the hope that these cluster species may provide a link between heterogenous and homogenous catalytic processes. Polynuclear metal chemistry also has relevance in the study of many metal-containing, biologically active enzymes and proteins. for example, attempts to mimic the action of the iron- and molybdenum-containing enzyme nitrogenase,[39] which reduces N_2 to NH_3, have centerd on the preparation of complexes having similar metal-ligand arrangements to that proposed for the active site of the enzyme.[40]

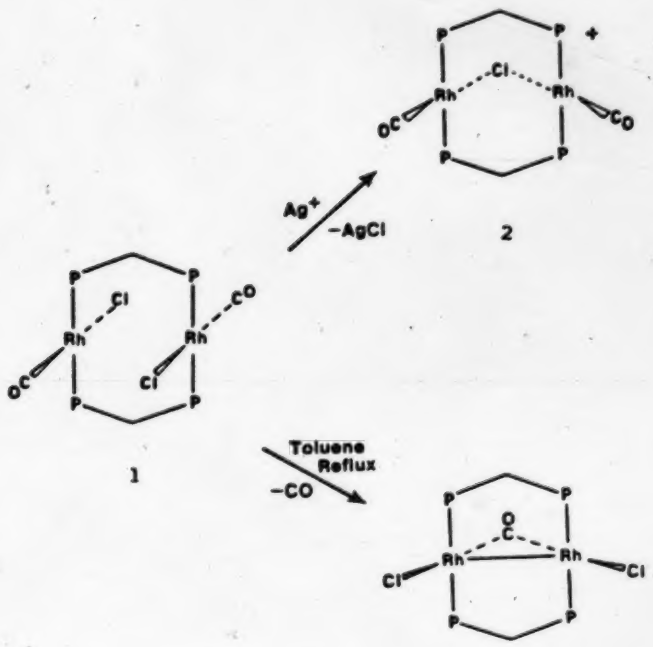
In order to utilize polynuclear metal complexes to the fullest extent, a thorough knowledge of the basic chemistry of these species must be obtained. To this end, studies have been undertaken of the reactions of well defined polynuclear systems in order to determine trends in the bonding modes and reactivities of various ligands. A convenient choice for such studies are binuclear complexes, containing two metal centers;[29] these are the simplest possible polynuclear systems, but still retain the possibility of metal cooperativity in the bonding and reactions of the ligands. The binuclear complexes usually employ inert bridging groups to hold the metals in close proximity throughout the reactions being studied. A wide

variety of bridging groups have been utilized, binding together a large assortment of metal fragments so the scope for diverse reactivity is large. However, the metal fragments are often closely related to well-studied mononuclear species thereby allowing the direct comparison of the chemistry of the binuclear and mononuclear systems.[28]

One such system is based on the compound trans-$[Rh_2Cl_2(CO)_2(DPM)_2]$ (**1**), the structure [41] of which is diagrammed below. This compound can be considered as two units of the mononuclear species trans-$[RhCl(CO)(PPh_3)_2]$[42] in a face-to-face arrangement, in which the trans triphenylphosphine ligands of the monomers have been replaced by the closely related bridging diphosphine ligand $Ph_2PCH_2PPh_2$ (DPM). The close structural similarities of the mononuclear and binuclear species as well as the known chemistry of the former suggest an interesting chemistry for the binuclear analogue **1**. Reactions of trans-$[RhCl(CO)(PPh_3)_2]$ have been studied for a number of reasons; not only is it a synthetic precursor in the preparation of the important hydroformylation catalyst $[RhH(CO)(PPh_3)_3]$,[43] but it is also closely related to two species which display a tremendous scope of reactivity with small molecules, namely $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$, known commonly as Wilkinson's compound and Vaska's compound, respectively. The former is a much studied catalyst for a

variety of reactions including the hydrogenation of olefins and the decarbonylation of aldehydes and acyl chlorides,[44] and the latter has yielded much valuable information regarding small molecule coordination and activation by metal complexes.[45]

Although in the binuclear complex **1** the metal centres are in close proximity, the important coordination site between the metals is not readily accessible, precluding simultaneous substrate activation by both metals unless substantial ligand movement occurs; only the vacant sites on the "outside" of the molecule are available to ligands. Nevertheless **1** has been found to display an extensive chemistry with small molecules such as CS_2,[46,47] SO_2,[48] and acetylenes.[22] In order to make the coordination sites between the metals more accessible to substrate molecules, **1** can be converted, by removal of a ligand, into species in which the two square planes of the rhodium coordination spheres share a corner. These are the so-called A-frame species, named because of the resemblance of their inner coordination spheres, viewed parallel to the metal-phosphine plane, to the letter A.[49] Two A-frame species which can be formed by ligand removal from **1** are shown below. Chloride abstraction from **1** yields the dicarbonyl cation, $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$, **(2)**,[50] and carbonyl removal from **1** yields the neutral monocarbonyl species, $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ **(3)**.[41]



1 2 3

Both 2 and 3 are coordinatively unsaturated, having 16 electron configurations at each metal as well as vacant and accessible coordination sites between the metals. The monocarbonyl species 3 has been found to be much more reactive than either 1 or 2, due in part to the presence of its metal-metal bond. Whereas reaction of 2 with a two-electron donor such as CO occurs with concomitant formation of a metal-metal bond giving both metals 18 electron configurations,[51] similar reactions of 3 result in Rh-Rh bond cleavage, leaving the metals with 16 electron configurations and still able to undergo further reaction.

A variety of reactions of **3** involving Rh-Rh bond reactivity has therefore been observed. For example, the activated actylenes RCCR (R = CF_3, CO_2Me) insert into the metal-metal bond, yielding $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}RCCR)(DPM)_2]$,[22] in which the acetylenes are bound as cis-dimetallated olefins parallel to the metal-metal vector. The carbonyl ligand of these species can be removed to give the new acetylene-bridged A-frame species $[Rh_2Cl_2(\mu\text{-}RCCR)(DPM)_2]$,[51] which are related to **3**, and undergo further interesting reactions.[52] Reaction of **3** with the acids HX (X = Cl^-, BF_4^-, $p\text{-}CH_3C_6H_4SO_3^-$) also occurs, leading to protonation of the metal-metal bond and accompanying coordination of the acid anion at one of the metals.[53]

In addition, CS_2 reacts with **3**, eventually yielding $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$, in which the unusual C_2S_4 moiety has resulted from the condensation of two CS_2 units.[46,47] The first step in this reaction is most likely reaction of CS_2 at the metal-metal bond as observed for the above reactions of acetylenes and HX. Although examples of reactivity at the metal-metal bond in **3** have been documented, the factors which favour the involvement of both metal centres, rather than ligand coordination solely at one of the terminal sites remote from the bridging position, are not well understood. Furthermore, the current interest in the activation of molecules which are related to carbon

dioxide, and the previous work done within these laboratories on the chemistry of CS_2 with compound 3 suggested that a fruitful study would involve the chemistry of some other sulfur containing species, related to CS_2, with compound 3.

The aims of the studies described in this thesis are, therefore, twofold: to study the chemistry of compound 3 with some sulfur containing ligands, and to interpret the results of these studies in terms of the relevance to possible catalytic processes.

CHAPTER TWO

ISOTHIOCYANATE ACTIVATION BY TWO METAL CENTERS.

Introduction

The current need to develop alternative sources of hydrocarbons has provided an incentive for recent studies of the catalyzed reduction of carbon monoxide and carbon dioxide.[54,55] Of these two potential C_1 sources, the former has attracted by far the more interest, having been succesfully used, for example, in the Fischer-Tropsch synthesis since World War II.[56] However, the major source of CO for this reaction is coal, an already depleted and non-renewable resource. Carbon dioxide, on the other hand, is a largely untapped carbon source; it is readily available from vast deposits of carbonate rocks and as an end product of the combustion of organic matter. Therefore, the possibility of its conversions into hydrocarbons or other organic compounds is of obvious importance, since such transformations would not involve the use of conventional carbon sources.

In order to make use of CO_2 as a source of carbon for C_1 chemistry, methods must be found to activate it

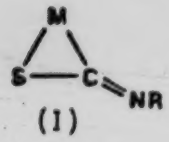
catalytically, since it is a rather unreactive molecule. The carbon atom of CO_2 is essentially electrophilic and the chemical exploitation of this resource require a supply of energy, usually in the form of electrons.[54,55] One approach to the problem that has been utilized by organometallic chemists, is to attempt to activate CO_2 to reaction by coordinating it to a metal center.[54,55] It is, therefore, important to obtain a thorough understanding of the coordination modes CO_2 in metal complexes and the reactions it can subsequently undergo.

Due to the general lack of reactivity of CO_2, few metal complexes of this molecule have been isolated.[57-59] Studies, instead, have tended to concentrate on the closely related heteroallenes (X=C=Y; X, Y = O, S, NR, CR_2) which, because of their greater reactivities with transition metal complexes, serve as useful model systems from which we can obtain information regarding the coordination modes and reactions of CO_2 itself.[55] The hope is that these studies will ultimately yield clues leading to the possible utilization of CO_2 in useful catalytic reactions.

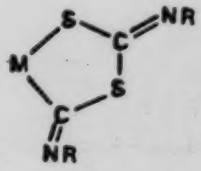
The chemistry of the heteroallenes, including CO_2, is also of interest for reasons other than that described above. These molecules are capable of being incorporated into organic substrates yielding products containing the heteroatoms of the respective heteroallene molecules. Such

reactions are typically metal-catalyzed and include the preparation of ethylene carbonate from ethylene oxide and CO_2, catalyzed by $[Ni(CO)_2(PCy_3)_2]$,[60] and the preparation of HR_2CCHO (R = H, Ph) from the reaction of R_2CCO with $[Mo_2(C_5H_4CH_3)_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)]$ followed by hydrogenation.[61] Other examples have also been reported.[60,62-64] Heteroallenes also display a wealth of interesting chemistry with transition metals in which many coordination modes and subsequent transformations are observed, some of which are described below.

One group of heteroallenes are the organic isothiocyanates (RN=C=S). These molecules have been found to undergo three distinct types of reaction with metal complexes. First, the molecules can bind to a metal via the carbon-sulfur double bond, forming a three membered M-C-S metallocycle.[65-72] This coordination mode, termed η^2 or π (see (I) below), although quite common for CS_2, is somewhat rarer for isothiocyanates and it is only recently that the first structure of a compound showing this bonding mode was reported.[72] Isothiocyanates may also undergo condensation reactions in which two,[68,80-83] or in one case, three molecules[68] are fused together and attached to the metals. Example II shows the structure of the more common product involving two isothiocyanate units.

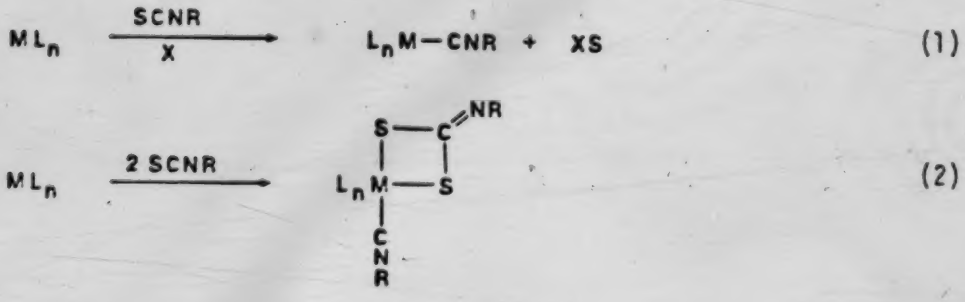


(I)



(II)

Most commonly, however, only the degradation products of isothiocyanates are observed in the final products. In the presence of a sulfur abstracting compound such as a phosphine, metal isocyanides and the corresponding sulfide are obtained[82-89] (Equation 1), or in the presence of excess isothiocyanate, a disproportionation reaction, yielding an isocyanide and a dithiocarbonimidato group, can occur (Equation 2).[65,70,71,81,90-95]



The disproportionation reaction can be readily envisaged as proceeding via a condensed species such as II above by C-S cleavage and M-S bond formation, and may result in products

in which the isocyanide and dithiocarbonimidato ligands remain coordinated to the same metal,[65,70,71,82] or products in which only one remains coordinated.[70,71,82,91-95]

All these coordination and reactivity modes have been observed for both CO_2 and the other heteroallenes in their reactions with metal complexes,[96-111] supporting the contention that heteroallenes such as isothiocyanates can function as useful models for the reaction of CO_2 itself.

Although several studies involving isothiocyanate activation by mononuclear complexes have been reported, few such reports pertaining to reactions with binuclear metal systems have appeared.[86] In order to determine the effects on isothiocyanate molecules by the action of two metal centres, an investigation of the reactions involving $[Rh_2X_2(\mu\text{-}CO)(DPM)_2]$ (X = Cl, I) was undertaken in the hope that the results of the study would widen our knowledge of the chemistry of isothiocyanates and, thus, CO_2 itself.

Experimental Section

All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen and reactions were routinely carried out under Schlenk conditions utilizing a dinitrogen atmosphere.

Bis(diphenylphosphino)methane (DPM) was purchased from Strem

Chemicals, hydrated rhodium trichloride from Research Organic/Inorganic Chemicals, methyl, phenyl-, and ethoxycarbonylisothiocyanate from Aldrich and benzoylisothiocyanate from ICN Pharmaceuticals. These and all other reagent grade chemicals were used as received. $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (**1**),[41] $[Rh_2I_2(\mu\text{-}CO)(DPM)_2]$ (**2**)[22] and CNMe[112] were prepared by the reported procedures. Infrared spectra were recorded on a Nicolet 7199 spectrometer with use of Nujol mulls on KBr plates, KBr discs, or in solution in KBr cells. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra were recorded on Bruker WP200, WP400 (at 161.93 MHz) and HFX-90 (at 22.6 MHz) instruments, respectively, unless otherwise noted. The phosphorus chemical shifts were measured relative to external H_3PO_4 whereas those for hydrogen and carbon are reported relative to tetramethylsilane. An internal deuterium lock (usually CD_2Cl_2) was used for all samples. For all nuclei, positive shifts are downfield from the standards. Elemental analyses were performed within the department or by Canadian Microanalytical Service Ltd., Vancouver, Canada. Conductivity measurements were performed using a Yellow Springs Instrument Model 31 and using approximately 1×10^{-3} M solutions in CH_2Cl_2. No conductivity was observed for any of the samples described in this Chapter.

Preparation of Compounds

(i) $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ (**3**): 500 mg of compound **1** (0.466 mmol) was dissolved in 4 mL of CH_2Cl_2 and ethoxycarbonylisothiocyanate (56 µL, 0.475 mmol) was added from a syringe causing the color of the solution to change to deep red, soon after which a light brown precipitate was deposited. The reaction mixture was stirred for 10 min, whereupon 5 mL of diethyl ether was added to complete precipitation. The product was isolated by filtration, washed repeatedly with ether to remove traces of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(C(O)OEt)_2)(DPM)_2]$ (vide infra), and dried in vacuo. This product and all other solids described in this paper are air stable and were routinely handled in air. Spectral and physical data for all new compounds are given in Tables 2 and 3. Yield, 79%.
Analysis. Calculated for $C_{55}H_{49}Cl_2NO_3P_4Rh_2S$: S, 54.8; H, 4.1; N, 1.2; Cl, 5.9; S, 2.7. Found: C, 54.2; H, 4.3; N, 1.2; Cl, 5.3; S, 2.9.

(ii) $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)Ph)(DPM)_2]$ (**4**): Compound **4** was prepared in a manner analogous to that of **3**, but using 500 mg of compound **1** and 65 µL of PhC(O)NCS (0.505 mmol). The tan solid isolated was washed with ether and dried in vacuo. Yield, 85%.

Table 2. Infrared Spectral Details for the Compounds Described in Chapter Two.

No.	Compd.	ν(CO), cm^{-1}	ν(^{13}CO), cm^{-1}	Others, cm^{-1}
3	$[Rh_2Cl_2(\mu\text{-}CO)(SCNC(O)OEt)(DPM)_2]$	1710 [a] 2023, 1717 [b]	1670 [a] 1977, 1676 [b]	
4	$[Rh_2Cl_2(\mu\text{-}CO)(SCNC(O)Ph)(DPM)_2]$	1714 [a] 2010, 1718 [b]	1673 [a] 1971, 1678 [b]	
5	$[Rh_2I_2(CO)(SCNC(O)OEt)(DPM)_2]$	2001 [a] 2001 [b]		
6	$[Rh_2Cl_2(CO)(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$	1968, 1700 [a]	1912, 1665	
8	$[Rh_2Cl_2(\mu\text{-}CO)(CNMe)(SCNC(O)OEt)(DPM)_2]$	1668 [a] 1668 [b]	1625 [a]	2229 [a,c] 2216 [b,c]
9	$[Rh_2Cl_2(\mu\text{-}CO)(CNMe)(SCNC(O)Ph)(DPM)_2]$	1656 [a] 1656 [b]	1621 [a]	2229 [a,c] 2220 [b,c]
10	$[Rh_2Cl_2(CO)(CNPh)(DPM)_2]$	1971 [a]		2165 [a,c]
11	$[Rh_2Cl_2(CO)(CNMe)(DPM)_2]$	1970 [a]		2169 [a,c]
12	$[Rh_2Cl_2(CO)(SCNC(S)N(C(O)OEt)_2)(DPM)_2]$	2026 [a]	1980 [a]	1772 [a,d], 1711 [a,d]
13	$[Rh_2Cl_2(CO)(SCNC(S)N(Me)C(O)OEt)(DPM)_2]$	2024 [a]	1974 [a]	1724 [a,d]
14	$[Rh_2Cl_2(CO)(SCNC(S)N(Ph)C(O)OEt)(DPM)_2]$	2022 [a]	1976 [a]	1739 [a,d]
15	$[Rh_2Cl_2(CO)(SCNC(S)N(C(O)Ph)C(O)OEt)(DPM)_2]$	2027 [a]	1980 [a]	1771 [a,d], 1673 [a,e]
16	$[Rh_2Cl_2(CO)(SCNC(S)SC(O)OEt)(DPM)_2]$	2023 [e]	1977 [a]	1769 [a,d]

a KBr disc

b CH_2Cl_2 solution

c absorption due to CNR

d absorption due to the unbound carbonyl of the EtOC(O) group.

e absorption due to the unbound carbonyl of the PhC(O) group.

Table 3. NMR Spectral Details for the Compounds Described in Chapter Two

Compound	^1H, δ, ppm	$^{13}C\{^{31}P(^1H)\}$, δ, ppm	$^1J_{Rh-C}$, Hz	$^{31}P\{^1H\}$, δ, ppm	$^1J_{Rh-P}$, Hz
3	2·64(q,2H), 0·70 (t,3H)[a,b] 4·14(m,2H), 3·21 (m,2H)[c]	199·0(br)		12·0(br)	
4	4·14(m,2H), 3·29 (m,2H)[c]	197·6(br)		11·6(br)	
5	4·20(q,2H), 0·67 (t,3H)[b] 4·90(m,2H), 4·65 (m,2H)[c]	197·5(d)	64·8	6·6(m) -0·6(m)	135·4 142·5
6		228·6(t) 191·5(d)	45·0 70·1	8·6(m) 5·3(m)	126·2 119·2
8	3·43(q,2H), 0·67 (t,2H)[b] 4·55(m,2H), 2·62 (m,2H)[c] 3·19(s,3H)[d]	232·0(d)	23·9,33·1	18·5(m) 6·0(m)	115·6 132·8
9	4·50(m,2H), 2·65 (m,2H)[c] 3·17(s,3H)[d]	234·8(d)	22·9,33·2	18·2(m) 6·0(m)	118·3 132·3
12	4·30(q,2H), 3·89(s,2H), 1·33 (t,3H), 1·08 (t,3H)[b] 4·38(m,2H), 4·14(m,2H)[c]	191·5(d)	70·4	8·2(m) 3·7(m)	99·1 92·6
13	4·12(q,2H), 1·22(t,3H)[b] 4·35(m,2H), 4·20(m,3H)[c] 2·89(s,3H)[e]	191·6(d)	69·4	9·8(m) 3·3(m)	107·0 96·0
14	4·06(q,2H), 1·06(t,3H)[b] 4·34(m,2H), 4·14(m,2H)[c]	191·5(d)	69·5	7·2(m) 2·0(m)	107·9 95·7
15	4·30(q,2H), 0·88(t,3H)[b] 4·38(m,2H), 4·12(m,2H)[c]	191·1(d)	73·0	7·2(m) 3·3(m)	99·3 93·0
16	4·34(s,2H), 1·34(t,3H)[b] 4·40(m,2H), 4·14(m,2H)[c]	191·0(d)	71·8	7·7(m) 3·9(m)	100·3 93·2

Footnotes

(a) Abbreviations used: q, quartet; t, triplet; m, multiplet; br, broad; d, doublet; dd, doublet of doublets.

(b) Resonances attributable to the isothiocyanate ethyl group.

(c) Resonances due to DPM methylene protons.

(d) Resonances due to MeNC.

(e) Resonance due to isothiocyanate methyl group.

Analysis. Calculated for $C_{59}H_{49}Cl_2NO_2P_4Rh_2S$: C, 57.3; H, 4.0; N, 1.1; Cl, 5.7; S, 2.6. Found: C, 56.5; H, 4.0; N, 1.1; Cl, 6.0; S, 2.7.

(iii) $[Rh_2I_2(CO)(\mu\text{-SCNC(O)OEt})(DPM)_2]$ (**5**): Compound **2** (100 mg, 0.080 mmol) was dissolved in 2 mL of CH_2Cl_2. Addition of 9.5 µL of EtOC(O)NCS (0.081 mmol) caused a change in color of the reaction to red-purple, from which a precipitate was obtained by addition of 10 mL of hexane. The red-purple solid was filtered, washed with hexane and dried in vacuo.

(iv) $[Rh_2Cl_2(CNMe)(\mu\text{-CO})(\mu\text{-SCNC(O)OEt})(DPM)_2]$ (**8**): 100 mg of compound **3** (0.083 mmol) was suspended in 3 mL of CH_2Cl_2 and 4.4 µL of MeNC (0.08 mmol) was added by syringe. The solid dissolved giving a red solution. Addition of 10 mL of diethyl ether precipitated a yellow solid which was filtered, washed with ether and dried in vacuo. Yield, 85%.
Analysis. Calculated for $C_{57}H_{52}Cl_2N_2O_3P_4Rh_2S$: C, 55.0; H, 4.2; N, 2.2. Found: C, 54.8; H, 4.4; N, 2.5.

(v) $[Rh_2Cl_2(CNMe)(\mu\text{-CO})(\mu\text{-SCNC(O)Ph})(DPM)_2]$ (**9**): Compound **9**, as a yellow solid, was obtained as described for compound **8** except using 100 mg (0.081 mmol) of compound **4** and 4.4 µL of MeNC (0.08 mmol). Yield, 80%.

Analysis. Calculated for $C_{61}H_{52}Cl_2N_2O_2P_4Rh_2S$: C, 57.3; H, 4.1; N, 2.2. Found: C, 56.6; H, 4.1; N, 2.3.

(vi) $[Rh_2Cl_2(CO)(CNPh)(DPM)_2]$ (**10**): Compound **1** (100 mg, 0.083 mmol) was dissolved in 5 mL of CH_2Cl_2. PhNCS (12.6 µL, 0.105 mmol) was added via syringe and the resulting red solution was stirred for circa 2 h. After standing for 24 h, a solid began to precipitate, which, after standing for several days, was collected by filtration and washed with ether. The yield of yellow solid was only circa 20%.

(vii) $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(C(O)OEt)_2)(DPM)_2]$ (**12**): Method (a). Compound **1** (100 mg, 0.093 mmol) was dissolved in 3 mL of CH_2Cl_2 and EtOC(O)NCS (50 µL, 0.415 mmol) was added by syringe. The color of the solution changed to orange immediately. Addition of 10 mL of hexane precipitated a yellow-orange solid which was isolated by filtration, washed with hexane and dried in vacuo. Method (b). Compound **3** (100 mg, 0.083 mmol) was suspended in 3 mL of CH_2Cl_2 and EtOC(O)NCS (10 µL, 0.085 mmol) was added by syringe. The solid dissolved within a minute yielding a clear orange solution. Addition of hexane precipitated compound **12** which was isolated as described above. Yield, 72%.

Analysis. Calculated for $C_{59}H_{54}Cl_2N_2O_5P_4Rh_2S_2$: C, 53.0; H, 4.1; N, 2.1; S, 4.8. Found: C, 52.1; H, 4.4; N, 1.9; S, 5.0.

(viii) $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Me)C(O)OEt)(DPM)_2]$ (**13**): To a suspension of **3** (100 mg, 0.083 mmol) in 3 mL of CH_2Cl_2 was added MeNCS (0.3 mL, 4.4 mmol). The solid dissolved giving an orange solution, from which a solid was precipitated by addition of 10 mL of hexane. Yellow-orange samples of **13** were isolated by filtration, washed with hexane and dried in vacuo. Yield, 75%.
Analysis. Calculated for $C_{57}H_{52}Cl_2N_2O_3P_4Rh_2S_2$: C, 53.6; H, 4.1; N, 2.2. Found: C, 53.2; H, 4.1; N, 2.5.

(ix) $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)XC(O)OEt)(DPM)_2]$ (X = NPh (**14**), NC(O)Ph (**15**); S (**16**)). Orange samples of compounds **14**, **15** and **16** were prepared as described for **13** but reacting compound **3** (100 mg, 0.083 mmol) with 0.2 mL of PhNCS (1.67 mmol), PhC(O)NCS (1.49 mmol) or CS_2 (3.3 mmol), respectively. Yields. **14**, 85%; **15**, 82%; **16**, 90%.
Analysis. (i) **14**. Calculated for $C_{62}H_{54}Cl_2N_2O_3P_4Rh_2S_2$: C, 55.6; H, 4.1; N, 2.1; S, 4.8. Found: C, 55.9; H, 4.3; N, 2.1; S, 5.1. (ii) **15**. Calculated for $C_{63}H_{54}Cl_2N_2O_4P_4Rh_2S_2$: C, 55.3; H, 4.0; N, 2.0; Cl, 5.2; S, 4.7. Found: C, 54.7, H, 4.3; N, 1.9; Cl, 5.3; S, 4.8.

(iii) **16**. Calculated for $C_{56}H_{49}Cl_2NO_3P_4Rh_2S_3$: C, 52.5; H, 3.9; N, 1.1; S, 7.5. Found: C, 52.2; H, 4.1; N, 1.2; S, 6.9.

Reaction of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ with CO.

Compound **3** (100 mg, 0.083 mmol) was suspended in 2 mL of CH_2Cl_2 in a three-necked, 50 mL round bottom flask and the dinitrogen atmosphere was replaced by CO. After stirring for 5 min the solids had dissolved yielding a yellow solution. Addition of 10 mL of diethyl ether resulted in the precipitation of a yellow solid which appeared from its infrared and ^1H and $^{31}P\{^1H\}$ NMR spectra to be a mixture of $[Rh_2Cl_2(CO)(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ (**6**) and $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPM)_2][Cl]$,[57] (**7**).

Reaction of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(O)Ph)(DPM)_2]$ with CO.

Reacting compound **4** with CO in the manner described for compound **3** yielded only **7**. Monitoring the reaction at intermediate times showed the presence of compounds **4** and **7**, but showed no indication of a compound analogous to **6**.

Attempted Reactions of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ with MeNCO, PhNCO, Allene and CO_2.

Compound **3** (50 mg, 0.042 mmol) was suspended in 5 mL of CH_2Cl_2. The reagents were added by syringe for the liquids, MeNCO (0.5 mL, 8.1 mmol) and PhNCO (0.5 mL, 4.6 mmol) or by replacing the N_2 atmosphere in the 50 ml flask by either allene or CO_2. No reaction was observed after 24 h in any of the reactions and compound **3** was recovered quantitatively.

Preparation of ^{13}CO Labelled Samples.

^{13}CO labelled samples of compounds **3-16** were prepared exactly as described previously but utilizing ^{13}CO labelled compounds **1** and **2** on an atmosphere of ^{13}CO for **6**.

X-ray Data Collection.

Orange crystals of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)\text{-}(DPM)_2]\cdot 0.5\ C_7H_8$ were grown from a saturated toluene solution of the complex. A suitable crystal was mounted on a glass fibre with epoxy resin. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 16 reflections in the range $4.0° \leq 2\theta \leq 17.0°$, which were

accurately centered or an Enraf-Nonius CAD4 diffractometer using Mo K_α radiation. The 2/m diffraction symmetry and the systematic absences (h0ℓ; ℓ = 2n+1: 0k0; k = 2n+1) were consistent with the space group $P2_1/c$.

Intensity data were collected at 22°C on a CAD4 diffractometer in the bisecting mode employing the ω-2θ scan technique. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of 2 standard reflections were measured every 1 h of exposure to assess possible crystal decomposition or movement. No significant variation in these standards was noted so no correction was applied to the data. 10,082 unique reflections were measured and processed in the usual manner using a value of 0.04 for p.[113] Of these, only 2112 were considered to be observed and were used in subsequent calculations. See Table 4 for pertinent crystal data and details of intensity collection.

Structure Solution and Refinement.

The structure was solved in the space group $P2_1/c$ by using a sharpened Patterson synthesis to locate the two independent rhodium atoms. Subsequent refinements and difference Fourier calculations led to the location of all the remaining non-hydrogen atoms. Atomic scattering factors

Table 4. Summary of Crystal Data and Details of Intensity Collection for $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]\cdot 0.5C_7H_8$

Cmpd	$[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]\cdot 0.5C_7H_8$
FW	1385·93
Space group	$P2_{1/c}$ (No. 14)
a, Å	17·964(9)
b, Å	25·235(10)
c, Å	15·861(5)
β, deg	97·02(3)
ρ calcd, g/m^3	1·29
V, Å^3	7136
radiatn	Mo Kα , $\bar{\lambda}$ = 0·709 260
detector aperture, mm	2·00 + 0·500 tanθ x 4
2θ limits, deg	0·1 ≤ 2θ ≤ 45·0
Scan type	ω/2θ
Scan width, deg	0·75 + 0·35 tanθ in ω
bkgd	25% on low and high angle sides
rflctns measd	±h, ±k, +ℓ, 10082
abs coeff μ, cm^{-1}	7·168
Crystal dimens, mm	0·05 x 0·10 x 0·11
range in abs corr factors	0·918 - 0·969
final no. of parameters varied	247
error in obs of unit weight	2·04
R	0·070
R_w	0·095

usual sources. Anomalous dispersion[116] terms for Rh, Cl, S and P were included in F_c. The carbon atoms of all phenyl groups were refined as rigid groups having D_{6h} symmetry and C-C distances of 1.392 Å; the isotropic thermal parameter for each of these carbon atoms was refined. All phenyl hydrogen atoms, as well as the DPM and ethyl methylene hydrogen atoms were included in their idealized locations (utilizing C-H distances of 0.95 Å) and were not refined. These atoms were assigned thermal parameters of 1 $Å^2$ greater than the B (or equivalent isotropic B) of their attached carbon atom. Absorption corrections were applied to the data using Gaussian integration.[117]

The large thermal parameters of the carbon atoms of the ethyl group suggested a possible disorder of these atoms so they were removed from the refinement and structure factor calculations. However, a subsequent difference Fourier map confirmed their positions and showed that the electron density associated with them was rather smeared out. These atoms were reinserted and refined as previously, resulting in large thermal parameters for these groups. It is probable that the ethyl groups are disordered over a number of closely spaced positions rather than over a few clearly defined positions.

The toluene molecule of solvation was found to be severely disordered about the 2(d) inversion centers.

Although the electron density was clearly attributable to a planar group of approximately D_{6h} symmetry the peak maxima corresponding to the individual carbon positions of the aryl ring were not clearly resolved; instead an almost continuous disk of electron density was observed. Similarly, no distinct positions were apparent for the toluene methyl group. Initially the toluene aryl group was input as a rigid group (in which only the three unique positions were defined) fixed at the inversion center, with an orientation corresponding to the "best" carbon positions from the Fourier map. The occupancy factor of this group was varied but indicated that a full molecule occupied this special position so the occupancy was set at 1.0 in subsequent cycles. A difference Fourier map at this point did not establish the positions of the toluene methyl group so its position was idealized such that it was 6-fold disordered around the ring. Neither the positions nor the thermal parameters of these carbons were refined, instead their B's were set at 1.0 A^2 greater than those of their attached aryl carbon atom. Another area of electron density was located in a position isolated from the complex and the solvent molecules, however this could not be adequately described as a solvent molecule so was left unaccounted for in the final refinements.

The final model, in space group $P2_1/c$, refined to R = 0.070 and R_w = 0.095 based on 247 parameters varied and 2112 unique observations. No doubt the very badly behaved toluene molecule of crystallization and the unaccounted for electron density together account for the rather high R values. Because of the small, weakly diffracting crystal only a small (ca. 21%) percentage of reflections collected were observed so only Rh(1), Rh(2), Cl(1), Cl(2), S(1), S(2), C(7) and C(8) were refined anisotropically in order to achieve a reasonable data/parameter ratio. On the final difference Fourier map the highest residuals were in the vicinity of the unaccounted for solvent (0.8 $eÅ^{-3}$), the carboxyethyl group (0.4 $eÅ^{-3}$) and the toluene molecule (0.4 $eÅ^{-3}$). A typical carbon in earlier syntheses had a density of ca. 3.0 $eÅ^{-3}$.

The final positional and thermal parameters for the non-group and group atoms are given in Tables 5 and 6, respectively. The idealized positional and thermal parameters for the hydrogen atoms are given in Table 7. Selected bond lengths and angles are listed in Tables 8 and 9, respectively. Least-squares planes calculations are recorded in Table 10. A listing of the observed and calculated structure factors amplitude is available.[118]

Table 5. Atomic Positional and Thermal Parameters for

$[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]\cdot 0.5\ C_7H_8$

Atom	x	y	z	U11	U22	U33	U12	U13	U23
Rh1	2055 (2)	-1414 (1)	1811 (2)	358 (21)	423 (23)	224 (20)	-8 (21)	48 (16)	50 (20)
Rh2	2551 (2)	-689 (1)	665 (2)	458 (24)	388 (23)	262 (21)	-33 (22)	107 (18)	29 (20)
Cl1	3121 (5)	-2020 (4)	1729 (6)	443 (73)	461 (78)	453 (75)	86 (60)	75 (59)	-18 (60)
Cl2	2644 (6)	157 (4)	-304 (6)	781 (89)	536 (84)	371 (70)	-134 (67)	108 (63)	132 (60)
S1	1381 (6)	-396 (4)	1071 (6)	541 (79)	305 (68)	382 (72)	21 (61)	226 (61)	118 (57)
S2	1318 (5)	-1822 (4)	2733 (6)	444 (75)	389 (73)	285 (68)	10 (61)	117 (56)	93 (56)
C7	-1254 (32)	-2363 (21)	3875 (49)	1139 (522)	759 (446)	4111 (1044)	542 (374)	1962 (618)	1454 (539)
C8	-1836 (40)	-2145 (33)	4299 (71)	1556 (753)	2412 (1000)	6681 (1800)	866 (689)	2443 (899)	2637 (1151)
P1	2797 (6)	-1042 (4)	2986 (6)	364 (32)					
P2	3279 (6)	-249 (4)	1755 (7)	443 (35)					
P3	1353 (6)	-1891 (4)	743 (6)	356 (31)					
P4	1586 (6)	-1139 (4)	-527 (7)	401 (32)					
O1	3910 (14)	-1320 (10)	406 (15)	905 (81)					
O2	-33 (15)	-2308 (11)	3146 (16)	620 (89)					
O3	-904 (17)	-1832 (12)	3651 (19)	855 (103)					
N1	641 (15)	-935 (11)	2103 (17)	340 (86)					
N2	-33 (16)	-1435 (13)	2989 (17)	461 (90)					
C1	3431 (21)	-1062 (15)	521 (23)	436 (119)					
C2	3566 (19)	-715 (14)	2602 (21)	427 (110)					
C3	1778 (19)	-1815 (14)	-272 (22)	440 (117)					
C4	1273 (18)	-892 (12)	1713 (20)	222 (96)					
C5	612 (16)	-1358 (13)	2568 (19)	177 (89)					
C6	-305 (27)	-1910 (21)	3307 (29)	767 (155)					

"Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. The positional and thermal parameters have been multiplied by 10^4. $U_{ij}=B_{ij}/(2\ a^*_i a^*_j)$ Å^2. The thermal ellipsoid is given by $\exp(-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl))$

Table 6. Derived Parameters for the Rigid Groups of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]\cdot 0.5C_7H_8$

Atom	x	y	z	B, Å²	Atom	x	y	z	B, Å²
C(11)	0.3244(15)	-0.1536(8)	0.3735(13)	2.5(8)	C(61)	0.0322(10)	-0.1775(11)	0.0604(15)	4.0(9)
C(12)	0.3942(14)	-0.1756(11)	0.3654(14)	5.6(11)	C(62)	0.0018(14)	-0.1336(9)	0.0157(14)	3.8(9)
C(13)	0.4261(11)	-0.2119(11)	0.4253(19)	5.9(11)	C(63)	-0.0747(15)	-0.1234(8)	0.0107(14)	3.8(9)
C(14)	0.3862(15)	-0.2262(9)	0.4932(15)	4.8(10)	C(64)	-0.1209(9)	-0.1571(11)	0.0503(16)	3.6(9)
C(15)	0.3184(15)	-0.2043(10)	0.5013(13)	3.6(9)	C(65)	-0.0905(15)	-0.2010(9)	0.0950(16)	5.9(12)
C(16)	0.2864(11)	-0.1679(9)	0.4414(17)	3.3(9)	C(66)	-0.0139(16)	-0.2113(8)	0.1001(14)	4.0(10)
C(21)	0.2472(16)	-0.0564(8)	0.3703(15)	3.2(9)	C(71)	0.2634(11)	-0.1244(10)	-0.1327(12)	3.5(9)
C(22)	0.1793(14)	-0.0299(11)	0.3515(13)	4.2(10)	C(72)	0.2959(14)	-0.1728(8)	-0.1496(14)	2.7(9)
C(23)	0.1580(12)	-0.0085(10)	0.4069(19)	7.0(13)	C(73)	0.3427(13)	-0.1763(8)	-0.2131(16)	4.9(11)
C(24)	0.2047(17)	0.0203(9)	0.4812(16)	3.7(9)	C(74)	0.3571(12)	-0.1315(11)	-0.2597(13)	3.8(9)
C(25)	0.2726(15)	-0.0063(11)	0.5000(13)	5.6(12)	C(75)	0.3246(14)	-0.0832(9)	-0.2428(14)	4.3(10)
C(26)	0.2938(11)	-0.0446(10)	0.4445(18)	4.8(11)	C(76)	0.2778(13)	-0.0797(8)	-0.1793(16)	4.3(9)
C(31)	0.2947(16)	0.0342(8)	0.2212(18)	3.5(9)	C(81)	0.1169(11)	-0.0871(10)	-0.1178(14)	2.8(9)
C(32)	0.3274(12)	0.0511(11)	0.3007(18)	5.7(12)	C(82)	0.0931(13)	-0.0353(9)	-0.1078(13)	2.7(8)
C(33)	0.3023(17)	0.0973(12)	0.3362(13)	6.1(12)	C(83)	0.0269(14)	-0.0173(7)	-0.1538(16)	3.8(10)
C(34)	0.2444(18)	0.1265(9)	0.2921(20)	7.7(14)	C(84)	-0.0155(11)	-0.0512(11)	-0.2098(14)	4.4(10)
C(35)	0.2116(13)	0.1096(11)	0.2126(20)	7.3(13)	C(85)	0.0083(14)	-0.1031(10)	-0.2199(14)	4.5(10)
C(36)	0.2368(15)	0.0635(12)	0.1772(13)	4.9(10)	C(86)	0.0745(15)	-0.1210(7)	-0.1739(17)	5.1(11)
C(41)	0.4185(12)	-0.0035(12)	0.1464(15)	3.4(9)	C(91)	-0.0495(14)	-0.0962(8)	0.3019(16)	2.6(8)
C(42)	0.4792(18)	-0.0381(8)	0.1496(16)	4.9(11)	C(92)	-0.1169(15)	-0.0906(9)	0.2494(13)	3.8(10)
C(43)	0.5465(13)	-0.0210(12)	0.1238(18)	6.7(13)	C(93)	-0.1614(11)	-0.0460(12)	0.2565(15)	5.4(11)
C(44)	0.5531(12)	0.0306(13)	0.0947(17)	6.2(12)	C(94)	-0.1384(14)	-0.0071(8)	0.3162(18)	4.5(10)
C(45)	0.4924(18)	0.0652(8)	0.0915(16)	6.1(12)	C(95)	-0.0709(16)	-0.0127(9)	0.3687(14)	4.7(10)
C(46)	0.4251(14)	0.0481(10)	0.1173(16)	3.9(10)	C(96)	-0.0264(11)	-0.0573(11)	0.3615(14)	4.7(10)
C(51)	0.1363(15)	-0.2609(7)	0.0825(19)	3.8(10)	C(101)	0.4910(29)	-0.0441(19)	0.5504(39)	18(3)
C(52)	0.0975(13)	-0.2070(12)	0.0133(14)	5.9(12)	C(102)	0.5155(27)	-0.0504(13)	0.4711(46)	18(2)
C(53)	0.0942(13)	-0.3421(13)	0.0122(15)	5.4(11)	C(103)	0.5244(25)	-0.0063(32)	0.4207(14)	18(3)
C(54)	0.1297(16)	-0.3711(7)	0.0802(20)	5.4(11)	C(111)	0.4811(62)	-0.0930(41)	0.6062(83)	19
C(55)	0.1695(13)	-0.3449(11)	0.1499(15)	4.3(10)	C(112)	0.5326(57)	-0.1062(27)	0.4390(96)	19
C(56)	0.1718(12)	-0.2898(11)	0.1505(13)	2.8(8)	C(113)	0.5515(53)	-0.0132(68)	0.3328(31)	19

Rigid Group Parameters

Group	x_c [a]	y_c	z_c	Delta [b]	Epsilon	Eta
Ring 1	0.3563(9)	-0.1899(6)	0.4334(10)	1.471(20)	-2.500(17)	2.233(18)
Ring 2	0.2259(9)	-0.0181(6)	0.4257(10)	-1.751(20)	-2.609(17)	2.259(17)
Ring 3	0.2695(10)	0.0804(7)	0.2567(11)	1.380(28)	2.322(17)	0.707(25)
Ring 4	0.4858(10)	0.0136(7)	0.1206(9)	1.380(20)	-2.872(16)	-0.363(16)
Ring 5	0.1330(8)	-0.3160(7)	0.0814(11)	-1.624(35)	-2.154(14)	-0.014(33)
Ring 6	-0.0444(9)	-0.1673(6)	0.0554(9)	2.999(20)	-2.535(14)	0.077(18)
Ring 7	0.3103(8)	-0.1280(7)	-0.1962(9)	0.136(15)	2.962(15)	-0.945(14)
Ring 8	0.0507(9)	-0.0692(7)	-0.1638(9)	2.989(18)	2.709(15)	-0.480(15)
Ring 9	-0.0939(9)	-0.0517(6)	0.3090(9)	-1.090(23)	-2.427(15)	2.940(20)
Ring 10	0.5000	0.0000	0.5000	0.462(60)	-2.295(54)	-1.093(58)

a x_c, y_c and z_c are the fractional coordinates of the centroid of the rigid group.

b The rigid group orientation angles delta, epsilon and eta (radians) have been defined previously: La Placa, S.J.; Ibers, J.A. Acta Crystallogr. 1965, 18, 511.

Table 7. Derived Parameters for the Hydrogen Atoms of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]\cdot 0.5C_7H_8$

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
H(1C2)	0.3833	-0.0524	0.3064	4.3	H(52)	0.1961	-0.2717	0.1980	6.3
H(2C2)	0.3884	-0.0970	0.2403	4.3	H(53)	0.1917	-0.3644	0.1964	6.0
H(1C3)	0.2231	-0.2013	-0.0224	4.1	H(54)	0.1294	-0.4090	0.0787	5.9
H(2C3)	0.1436	-0.1956	-0.0720	4.1	H(55)	0.0715	-0.3607	-0.0374	5.2
H(1C7)	-0.0917	-0.2594	0.4188	16.7	H(56)	0.0759	-0.2680	-0.0358	3.7
H(2C7)	-0.1450	-0.2558	0.3345	16.7	H(62)	0.0104	-0.2410	0.1301	4.9
H(12)	0.2374	-0.1553	0.4459	6.4	H(63)	-0.1183	-0.2235	0.1227	5.1
H(13)	0.2917	-0.2164	0.5462	6.9	H(64)	-0.1695	-0.1492	0.0484	4.6
H(14)	0.4109	-0.2511	0.5341	5.9	H(65)	-0.0920	-0.0924	-0.0187	6.8
H(15)	0.4756	-0.2247	0.4217	4.4	H(66)	0.0367	-0.1099	-0.0113	5.0
H(16)	0.4213	-0.1636	0.3214	4.7	H(72)	0.2536	-0.0461	-0.1698	4.4
H(22)	0.3409	-0.0614	0.4574	4.9	H(73)	0.3352	-0.0523	-0.2738	6.3
H(23)	0.3045	0.0035	0.5497	7.3	H(74)	0.3896	-0.1338	-0.3011	4.9
H(24)	0.1893	0.0470	0.5179	4.7	H(75)	0.3624	-0.2093	-0.2244	5.2
H(25)	0.1105	0.0256	0.3938	6.4	H(76)	0.2808	-0.2031	-0.1204	5.4
H(26)	0.1469	-0.0393	0.3015	5.7	H(82)	0.0923	-0.1568	-0.1812	3.3
H(32)	0.2162	0.0503	0.1274	6.5	H(83)	-0.0182	-0.1260	-0.2595	5.2
H(33)	0.1740	0.1281	0.1867	6.9	H(84)	-0.0580	-0.0388	-0.2418	5.4
H(34)	0.2317	0.1581	0.3185	8.1	H(85)	0.0127	0.0176	-0.1458	6.0
H(35)	0.3314	0.1103	0.3910	8.2	H(86)	0.1232	-0.0132	-0.0675	6.0
H(36)	0.3736	0.0325	0.3317	6.0	H(92)	-0.0191	-0.1251	0.2967	4.7
H(42)	0.3721	-0.0138	0.1639	8.1	H(93)	-0.1333	-0.1163	0.2093	6.7
H(43)	0.3838	0.0728	0.1142	8.0	H(94)	-0.2087	-0.0417	0.2217	5.4
H(44)	0.4970	0.1008	0.0697	7.0	H(95)	-0.1699	0.0241	0.3217	5.6
H(45)	0.5985	0.0422	0.0749	4.6	H(96)	-0.0557	0.0153	0.4091	6.7
H(46)	0.5868	-0.0444	0.1246	3.8					

Table 8. Selected Interatomic Distances (Å) in $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)\text{-}(DPM)_2]\cdot 0.5C_7H_8$

(i) Bonding

Rh(1) - Rh(2)	2·799(4)	C(6) - O(3)	1·28(4)
Rh(1) - Cl(1)	2·464(9)	O(3) - C(7)	1·54(5)
Rh(2) - Cl(2)	2·559(10)	C(7) - C(8)	1·42(8)
Rh(1) - P(1)	2·350(11)	Rh(2) - C(1)	1·88(4)
Rh(1) - P(3)	2·322(11)	C(1) - O(1)	1·11(4)
Rh(2) - P(2)	2·319(11)	P(1) - C(2)	1·78(4)
Rh(2) - P(4)	2·329(11)	P(2) - C(2)	1·81(3)
Rh(2) - S(1)	2·373(10)	P(3) - C(3)	1·87(3)
Rh(1) - S(2)	2·331(9)	P(4) - C(3)	1·80(3)
Rh(1) - C(4)	1·92(3)	P(1) - C(11)	1·84(2)
S(1) - C(4)	1·64(3)	P(1) - C(21)	1·80(3)
C(4) - N(1)	1·36(3)	P(2) - C(31)	1·79(3)
N(1) - C(5)	1·30(3)	P(2) - C(41)	1·83(3)
C(5) - S(2)	1·72(3)	P(3) - C(51)	1·82(2)
C(5) - N(2)	1·42(3)	P(3) - C(61)	1·86(2)
N(2) - C(91)	1·46(4)	P(4) - C(71)	1·84(2)
N(2) - C(6)	1·41(5)	P(4) - C(81)	1·82(2)
C(6) - O(2)	1·16(5)		

(ii) Non-bonding.

Cl(1) - H(52)	2·793	Cl(2) - H(32)	2·740
Cl(2) - H(86)	2·657	Cl(2) - H(72)	2·823

Table 9. Selected Bond Angles (Deg) in $[Rh_2Cl_2(CO)$-$(\mu$-SCNC(S)N(Ph)C(O)OEt)$(DPM)_2]\cdot 0.5C_7H_8$

(i) Bond Angles

Rh(2) - Rh(1) - P(1)	93·4(3)	Cl(2) - Rh(2) - S(1)	90·2(3)
Rh(2) - Rh(1) - P(3)	93·0(2)	Cl(2) - Rh(2) - C(1)	104·0(11)
Rh(1) - Rh(2) - P(2)	91·4(3)	Rh(2) - C(1) - O(1)	174(3)
Rh(1) - Rh(2) - P(4)	93·9(3)	Rh(2) - S(1) - C(4)	96·6(12)
P(1) - Rh(1) - P(3)	172·2(4)	Rh(1) - C(4) - S(1)	115(2)
P(2) - Rh(2) - P(4)	171·3(4)	S(1) - C(4) - N(1)	121(2)
Cl(1) - Rh(1) - P(1)	85·5(3)	Rh(1) - C(4) - N(1)	123(2)
Cl(1) - Rh(1) - P(3)	89·8(3)	C(4) - N(1) - C(5)	114(3)
S(2) - Rh(1) - P(1)	89.4(4)	N(1) - C(5) - S(2)	124(2)
S(2) - Rh(1) - P(3)	85·9(4)	C(5) - S(2) - Rh(1)	93·9(11)
C(4) - Rh(1) - P(1)	97·4(10)	N(1) - C(5) - N(2)	118(3)
C(4) - Rh(1) - P(3)	88·3(10)	S(2) - C(5) - N(2)	118(2)
Cl(2) - Rh(2) - P(2)	86·2(4)	C(5) - N(2) - C(6)	129(4)
Cl(2) - Rh(2) - P(4)	91·1(4)	C(5) - N(2) - C(91)	114(2)
S(1) - Rh(2) - P(2)	94·7(4)	C(6) - N(2) - C(91)	117(2)
S(1) - Rh(2) - P(4)	93·5(4)	N(2) - C(6) - O(2)	119(5)
C(1) - Rh(2) - P(2)	85·7(11)	N(2) - C(6) - O(3)	112(5)
C(1) - Rh(2) - P(4)	87·0(11)	O(2) - C(6) - O(3)	129(5)
Rh(1) - Rh(2) - Cl(2)	160·4(3)	C(6) - O(3) - C(7)	111(4)
Rh(1) - Rh(2) - S(1)	70·6(2)	O(3) - C(7) - C(8)	97(5)
Rh(1) - Rh(2) - C(1)	95·2(10)	Rh(1) - P(1) - C(2)	107·6(11)
Rh(2) - Rh(1) - Cl(1)	93·4(2)	Rh(2) - P(2) - C(2)	108·9(12)
Rh(2) - Rh(1) - S(2)	161·2(3)	Rh(1) - P(3) - C(3)	109·3(12)
Rh(2) - Rh(1) - C(4)	77·7(9)	Rh(2) - P(4) - C(3)	111·1(12)
S(2) - Rh(1) - Cl(1)	105·3(3)	P(1) - C(2) - P(2)	113(2)
S(2) - Rh(1) - C(4)	83·6(10)	P(3) - C(3) - P(4)	114(2)

(ii) Torsion Angles

P(1) - Rh(1) - Rh(2) - P(2)	-2·3(3)	C(5) - N(2) - C(6) - O(2)	-9(5)
P(1) - Rh(1) - Rh(2) - P(4)	170·8(4)	C(5) - N(2) - C(6) - C(3)	180(3)
P(3) - Rh(1) - Rh(2) - P(2)	-178·0(4)	N(1) - C(5) - N(2) - C(91)	-15(3)
P(3) - Rh(1) - Rh(2) - P(4)	-4·8(4)	S(2) - C(5) - N(2) - C(91)	163(3)
S(1) - Rh(2) - Rh(1) - C(4)	0·0(9)	O(2) - C(6) - N(2) - C(91)	165(3)
Rh(1) - C(4) - S(1) - Rh(2)	0·0(11)	O(3) - C(6) - N(2) - C(91)	-6(4)
Rh(1) - C(4) - N(1) - C(5)	1(3)	C(7) - O(3) - C(6) - O(2)	2(5)
Rh(1) - S(2) - C(5) - N(1)	-4(2)	C(7) - O(3) - C(6) - N(2)	172(3)
N(1) - C(5) - N(2) - C(6)	159(3)	C(6) - O(3) - C(7) - C(8)	175(5)
S(2) - C(5) - N(2) - C(6)	-23(4)		

Table 10. Calculated Least Squares Planes for $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)\text{-}(DPM)_2]\cdot 0.5C_7H_8$

Plane No.	Equation
1	-0·4168X - 0·4872Y - 0·7674Z + 1·8273 = 0
2	-0·3394X - 0·5243Y - 0·7810Z + 1·5725 = 0
3	-0·3917X - 0·5126Y - 0·7641Z + 1·6550 = 0
4	-0·3856X - 0·5159Y - 0·7650Z + 1·6248 = 0
5	-0·3393X - 0·5091Y - 0·7625Z + 1·6913 = 0

Distances from Planes (Å)

Plane No.	Atom										
	Rh(1)	Rh(2)	C(1)	C(2)	S(1)	S(2)	N(1)	N(2)	C(1)	C(4)	C(5)
1	-0·014(3)	0·015(3)	0·02(1)	-0·11(1)	0·07(1)	0·00(1)			-0·02(3)	0·04(3)	
2					0·00(1)	0·00(1)	-0·02(2)	0·01(3)		-0·02(3)	0·01(3)
3	-0·002(3)	0·002(3)			-0·02(1)	0·00(1)	0·04(3)			-0·02(3)	0·09(3)
4	-0·003(3)	0·004(3)			-0·03(1)	0·00(1)	0·02(3)	0·14(3)		-0·03(3)	0·06(3)
5	0·000(3)	0·000(3)			0·00(1)					0·00(1)	

Description of Structure

The unit cell of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)\text{-}(DPM)_2]\cdot 0.5\ C_7H_8$ (**14**) consists of four discrete complex and two toluene molecules, the latter which are severely disordered about the 2(d) inversion centers. There are no unusual contacts between any of these molecules.

The overall geometry of the complex, shown in Figure 1, is quite typical for DPM bridged binuclear complexes, in that the bridging diphosphine ligands are bound in the mutually trans positions on each metal with the other ligands bound essentially perpendicular to the metal-phosphine plane.[49] Parameters within the Rh-DPM framework are not particularly unusual and are comparable to those observed in several related complexes already reported by this group.[41,46-53] The metal-metal separation (2.799(4) Å) is representative of a normal Rh-Rh single bond, falling within the range reported in related Rh-Rh bonded systems (2.7566(9)-2.8415(7) Å).[119,120] This metal-metal bond is substantiated by the intraligand P-P separations (av. 3.04(2) Å) which are significantly longer than the Rh-Rh separation suggesting mutual attraction of the metals. Inclusion of the metal-metal bond in describing the metal geometries yields a quasi-octahedral coordination about both metals much as was observed in the closely related CS_2 condensation product, $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$.[46,47] The

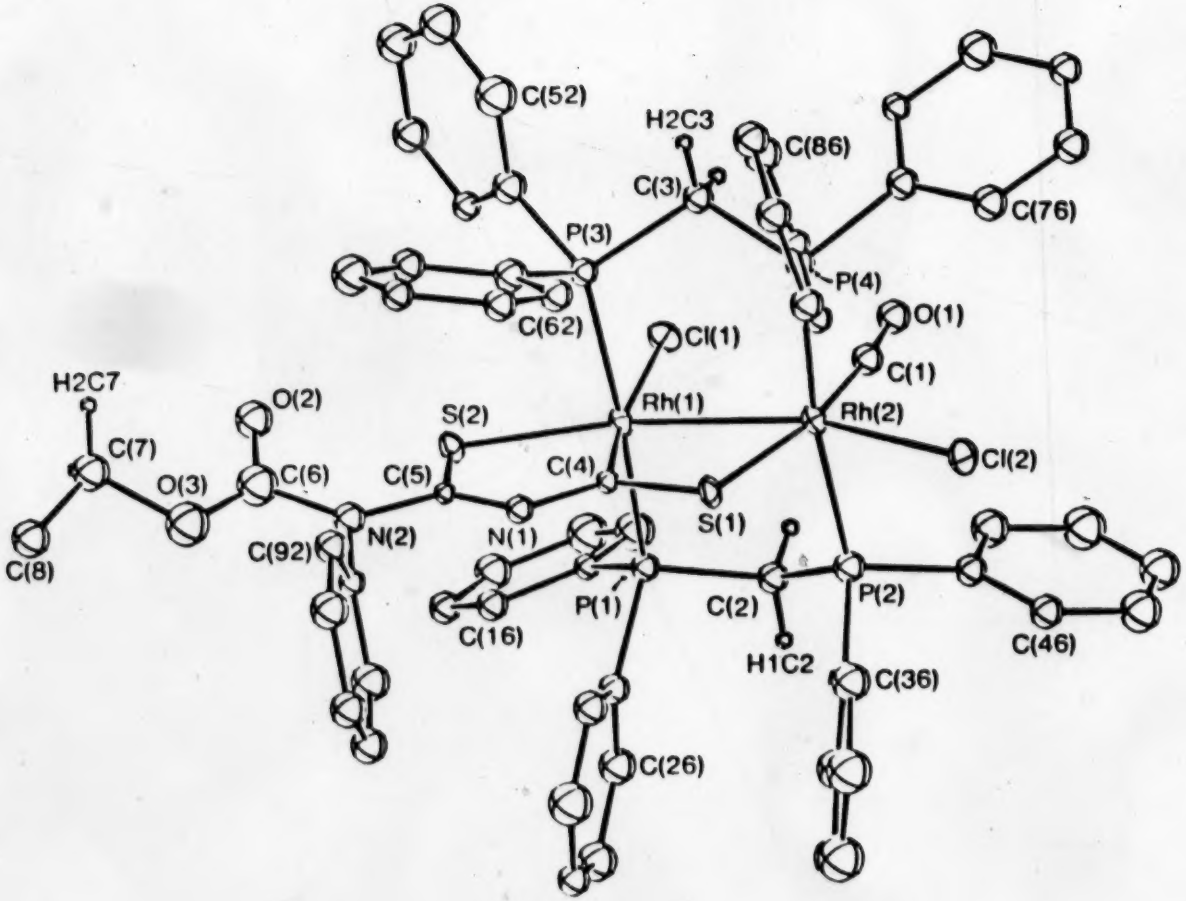


Figure 1. Perspective view of the $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]$ molecule showing the numbering scheme.

coordination geometry about Rh(1) is comprised of the mutually trans phosphorus atoms of the DPM ligands, a terminal chloro ligand, the Rh-Rh bond and two interactions with S(2) and C(4) of the bridging isothiocyanate moiety (vide infra), whereas the geometry about Rh(2) is comprised of the mutually trans phosphines, a terminal chloro and carbonyl ligand, the Rh-Rh bond and one interaction with S(1) of the isothiocyanate group. Distortions from ideal octahedral geometry of each Rh center seems to result primarily from the strain imposed by the bridging isothiocynate group.

Both terminal Rh-Cl distances are significantly longer than is normally observed for such bonds, for which distances such as those reported in trans-$[Rh_2Cl_2(CO)_2L_2]$ (L = $Ph_2PCH_2PPh_2$ (2.3875(9) Å),[41] $Ph_2AsCH_2AsPh_2$ (2.370(3) Å)[121]) are more typical. These Rh-Cl distances are, however, comparable to those observed in the closely related complex, $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$.[46,47] Thus, the Rh-Cl bond which is trans to the sigma-bound carbon atom in these compounds (Rh(1)-Cl(1) = 2.464(9) Å in **14**; 2.442 Å (av.) in the C_2S_4 analogue) displays the lengthening which is typical for Cl when opposite a group of high trans influence,[122] and the Rh(2)-Cl(2) bond which is opposite the Rh-Rh bond is extremely long in each case (2.559(10) Å in **14**; 2.518 Å (av.) in C_2S_4 analogue); it appears the only Rh-Cl distance

which is longer than that of compound **14** was observed in $[RhCl(\eta^1\text{-}CO_2)(diars)_2]$[59] (2.635(4) Å). While it may be that the metal-metal interaction in the present compound exerts a strong trans influence on the Rh(2)-Cl(2) bond, as has been suggested in a related complex,[123] steric interactions between the phenyl hydrogens and this Cl atom cannot be ruled out as being, at least in part, responsible. Phenyl groups 3, 7 and 8 are aimed into the regions around Cl(2) in such a way as to cause lengthening of the Rh(2)-Cl(2) bond (see Figure 1) and several short non-bonded contacts involve these hydrogens and Cl(2) (see Table 6). It is significant, however, that the longer Rh(2)-Cl(2) distance observed in the present case is accompanied by the shorter Rh-Rh bond (compared with 2.811(3) in the C_2S_4 analogue[46,47]) as would be expected were the trans influence of the Rh-Rh interaction responsible for the lengthening.

As noted, the coordination geometries about both metals are completed by the bridging group which has resulted from condensation and rearrangement of the original isothiocyanate ligands. This condensed fragment binds to the metals yielding one 5-membered and one 4-membered metallocycle as shown clearly in Figure 2. Therefore, the present complex looks much like the C_2S_4 analogue,[46,47] apart from CO_2Et and Ph moieties in the former. Otherwise, most differences between these two complexes seem to result

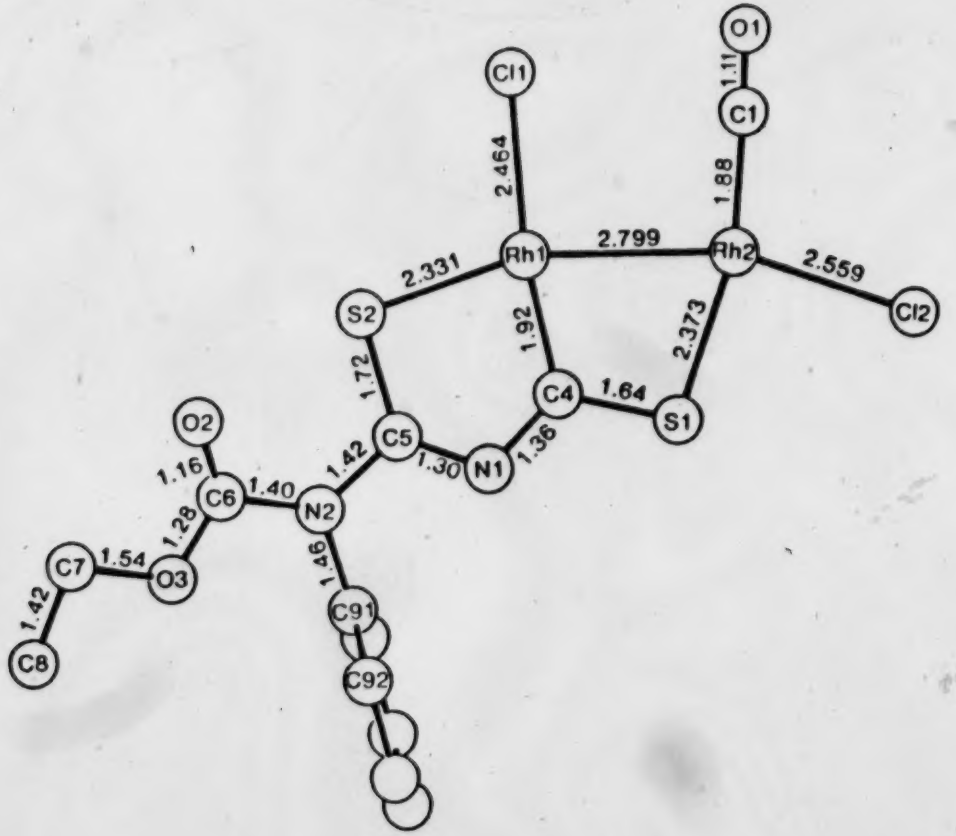


Figure 2. Inner coordination sphere of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]$ in the approximate plane of the metals and the isothiocyanate ligand.

from the smaller covalent radius of N compared to S, resulting, for example, in a smaller 5-membered ring in the isothiocyanate product.

The head-to-tail condensation of the EtOC(O)NCS and PhNCS groups, which resulted in formation of the N(1)-C(5) bond, has also been accompanied by migration of the ethoxycarbonyl moiety from N(1) to N(2), much as was observed in $[RhCl(PPh_3)_2(SC(N(C(O)OEt)_2NCSC(NC(O)OEt)S)]$,[68] in which a condensation of three SCNC(O)OEt groups occurred. This migration in the present compound has resulted in the formation of a new isothiocyanate group, SCNR (where R = C(S)N(Ph)C(O)OEt), which is bound between the two metals and is carbon bound to one rhodium center and sulfur-bound to the other, much as we propose for the initial 1:1 isothiocyanate adducts (vide infra), and similar to that observed for CS_2 in a binuclear platinum complex.[124] This is only the second reported structure involving an isothiocyanate group and is the first in which this group bridges two metals. Apart from the ethoxycarbonyl and phenyl groups, the metal isothiocyanate unit is quite planar; only N(2) is significantly displaced (0.14(3) Å) from the Rh(1)Rh(2)S(1)C(4)N(1)C(5)S(2)N(2) least-squares plane. Exo to the metallocycle rings significant twists from this plane occur, the torsion angles about the N(2)-C(5) and the N(2)-C(6) bonds being <u>circa</u> 19°

and 8°, respectively (see Table 7), allowing O(2) to avoid unfavourable contacts with S(2). In addition, the phenyl group is twisted from the least-squares by *circa* 87° in order to minimize contacts with the rest of the ligand. As was the case for the C_2S_4 analogue,[46,47] the parameters within the isothiocyanate unit suggest extensive delocalization.

One C-S bond (C(5)-S(2)) is similar in length to that in ethylene thiourea (1.72 Å),[125] whilst the other (C4-S1) is somewhat shorter. Neither, however, are as short as the double bonds in COS[126] and CS_2[127] (*circa* 1.55 Å). And the C-N bonds within the metallocycle (1.30(3) and 1.37(3) Å) are typical for partial double bond character and are much shorter than a typical C-N single bond (1.47 Å).[125] Two of the distances involving the exocyclic nitrogen atom N(2) are somewhat shorter than a normal single bond, although this difference is not significant; the N(2)-C(91) distance on the other hand is exactly as expected for a single bond.

The length of the bridging C-S bond in compound **14** (1.64(3) Å) is similar to that observed in the C_2S_4 product (1.66(3) Å) and also to that in the other structurally characterized isothiocyanate complex, $[Ni(CH_3C(CH_2PPh_2)_3)(\eta^2\text{-SCNPh})]$[79] (1.68(2) Å). Although the two isothiocyanate species differ in the coordination mode of the isothiocyanate ligands (the former is bridging

whereas the latter is η^2 bound), the C-S moiety seems to be rather insensitive to this difference.

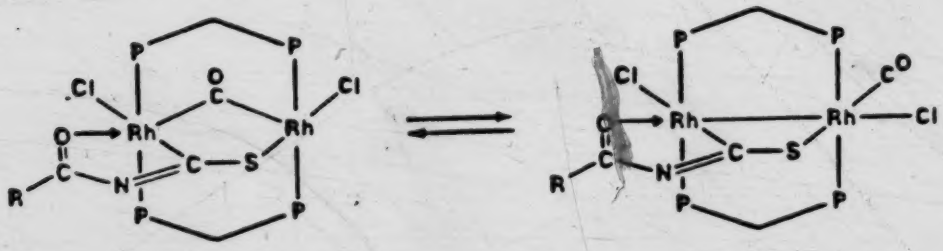
Discussion of Results

(i) The 1:1 Reactions of Compounds 1 and 2 with Isothiocyanates. The addition of an equimolar amount of either ethoxycarbonylisothiocyanate (SCNC(O)OEt) or benzoylisothiocyanate(SCNC(O)Ph) to compound 1 yields $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(O)R)(DPM)_2]$ (R = EtO (**3**), Ph (**4**)) in about 80% yield. Based on their elemental analyses, on a consideration of their spectral parameters and on their subsequent chemistry (vide infra) it can be established that in each case the isothiocyanate molecule has inserted into the Rh-Rh bond of compound 1. In the solid state neither compound shows a terminal carbonyl stretch but instead displays a medium intensity band at circa 1710 cm^{-1} which shifts to circa 1670 cm^{-1} when ^{13}CO-substituted compound 1 is used. The shift upon ^{13}CO-substitution clearly establishes that this stretch is not due to the isothiocyanate carbonyl group. In fact, no stretch clearly attributable to this organic carbonyl moiety is observed. The low carbonyl stretch, although unusual for a "conventional" carbonyl group, is well in line with those reported for carbonyl moieties which bridge two metals not

bonded to each other (ketonic carbonyls);[41] in the present case the ketonic carbonyl has resulted from isothiocyanate insertion into the Rh-Rh bond of **1**. The analogous insertion of acetylenes into the Rh-Rh bond of **1** to give ketonic carbonyl species is a well documented transformation.[41] I propose that in these complexes the isothiocyanate molecule is bridging the two metals and is bound to one through the S atom and to the other via the isothiocyanate carbon atom. A similar binding mode for the related CS_2 molecule has already been reported[124] (and again this has resulted from heteroallene insertion into a metal-metal bond) but more importantly the structure reported herein for compound **14** unambiguously establishes this bonding mode for an isothiocyanate molecule (vide supra). The absence of an observable stretch for the organic carbonyl moiety suggests that this carbonyl group is coordinated to the metal, and certainly the coordination of such carbonyl groups in benzoyl- and ethoxycarbonylisothiocyanates has been observed.[68,80,81]

In solution, the infrared spectra of compounds **3** and **4** show additional bands of 2023 and 2010 cm^{-1}, respectively, which disappear upon crystallization. These bands are close to those observed in compound **14** and in $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$ (2030 cm^{-1}),[46,47] indicating the presence of a terminal carbonyl ligand. The disappearance

of these bands upon crystallization and their reappearance in solution, together with the bridging carbonyl band, suggests the following equilibrium between the carbonyl-bridged species (A) and that containing a terminal CO group (B). The $^{31}P\{^{1}H\}$ NMR spectra of compounds **4** and **5** consist of broad unstructured signals in the region 11-12 ppm, which



(A) (B)

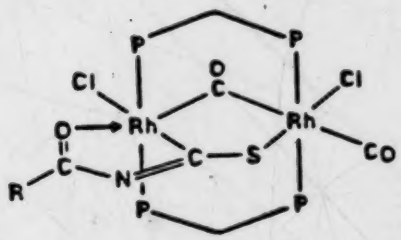
are temperature invariant over the range 20° to -80°C. Likewise the $^{13}C\{^{31}P\{^{1}H\}\}$ NMR spectra consist of a broad peak at <u>circa</u> 199 ppm; although this is normally the region associated with terminal carbonyl groups, the ^{13}C resonances of ketonic carbonyls have also been observed in this region.[41] Both sets of NMR spectra are consistent with the above dynamic behaviour. The ^{1}H NMR spectrum shows the DPM methylene resonances as broad unresolved patterns but with peak envelopes essentially as is normally seen in related DPM-bridged complexes, but, interestingly, the resonances due to the ethyl group are clearly resolved, presumably since this group is well removed from the sites affected by

the fluctionality. This structure proposed for isomer B is analogous to those observed for $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$[46,47] and compound **14**.

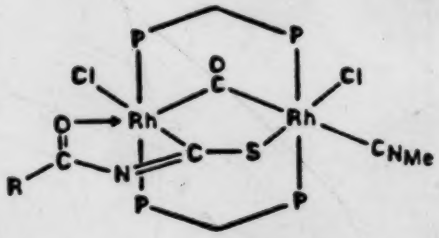
The iodo analogue of compound **1**, $[Rh_2I_2(\mu\text{-}CO)(DPM)_2]$ (**2**), also reacts with one equivalent of EtOC(O)NCS to yield $[Rh_2I_2(CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ (**5**), a species having only a terminal carbonyl stretch (2001 cm^{-1}) both in solid and solution. The $^{31}P\{^1H\}$ NMR spectrum of this product is well resolved AA'BB'XY pattern, which, together with the infrared spectrum and the lack of conductivity, suggests that it has a structure analogous to isomer B shown above for the chloro species. Complexes in which a bridging carbonyl ligand is not accompanied by a metal-metal bond are still not common[41,128-131] and the subtle factors which favour this carbonyl geometry are not yet understood, although it seems that slight changes, such as the exchange of Cl for I in compound **3** to give **5**, are enough to destabilize this carbonyl geometry. Such a change can be rationalized based on steric arguments; the larger iodo group on the more crowded rhodium center presumably forces the carbonyl group from the bridging position to the terminal site on the other metal.

The carbonyl-bridged forms of compounds **3** and **4** (isomer A) have a coordinatively unsaturated, 16 electron rhodium center suggesting the possibility of coordinating a

2-electron donor at this metal. Consequently, reacting a suspension of **3** in CH_2Cl_2 with CO yields a clear yellow solution, the $^{31}P\{^1H\}$ NMR spectrum of which shows the presence of two species **6** and **7** whose molar ratios vary with reaction time (vide infra). The first species, whose spectrum is typical of an AA'BB'XY spin system, appears to be a simple CO-adduct of **3** as diagrammed below. This species displays carbonyl stretches in an infrared spectrum of the solid at 1968 and 1700 cm^{-1} (1912 and 1665 cm^{-1} in ^{13}CO substituted product) and shows two resonances in the $^{13}C\ \{^1H\}$ NMR spectrum of an enriched sample, at 191.5 and 228.6 ppm, consistent with a terminal and a bridging carbonyl group. These ^{13}C resonances were not ^{31}P decoupled so the former appears as an approximate doublet of triplets (J_{Rh-C} = 70 Hz; $J_{P-C} \simeq 7$ Hz) and the latter is a complex multiplet which roughly appears as a broad triplet indicating that the coupling to both Rh centers is approximately the same ($J_{Rh-C} \simeq 43$ Hz). The second product (**7**) was identified as $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPM)_2][Cl]$[132] based on a comparison of its $^{31}P\{^1H\}$ $^{13}C\ \{^1H\}$ NMR and infrared spectra (ν(CO) = 2004, 1960 and 1868 cm^{-1}) with those of the same complex having either BPh_4^- or $RhCl_2(CO)_2^-$ anions.[133] Compound **6** could not be isolated pure since all samples were contaminated by compound **7** to varying degrees. In the reaction of the benzoylisothiocyanate



R = OEt (6)



R = OEt (8)
Ph (9)

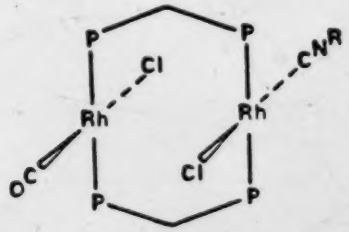
analogue 4 with CO no carbonyl adduct similar to 6 is observed; instead only starting material and the tricarbonyl species 7 appears. After prolonged exposure to CO only 7 is observed and ultimately both compounds 3 and 4 react under excess CO with isothiocyanate displacement to give compound 7. It appears that the coordinatively unsaturated, 16 electron rhodium center is required for the reaction with CO since the analogous species 14, which has a bridging isothiocyanate group but a terminal CO and therefore two 18 electron rhodium centers, is unreactive towards CO, presumably since the thiocarbonyl moiety is strongly bound to Rh(1). The iodo compound 5, which also has 18-electron configurations at both metals also does not react with CO. This is somewhat surprising since it would be expected that the coordinated carbonyl group of the isothiocyanate group would be readily displaced by carbon monoxide as has previously been reported in similar compounds[68] and as we propose occurs for the chloro analogue 3 (vide infra); it

seems that exchange of Cl for I markedly lowers the lability of this coordinated isothiocyanate carbonyl group.

Similarly, compounds **3** and **4** react with one equivalent of MeNC to give compounds **8** and **9**, respectively, in 100% yield (from NMR). These products have similar $^{31}P\{^{1}H\}$ NMR spectra to compound **6** and their infrared spectra show the presence of ketonic carbonyl groups (ν(CO) = 1667 cm^{-1} (**8**); 1656 cm^{-1} (**9**)) and terminal isocyanide ligands (ν(CN) = 2229 cm^{-1} (**8**) and (**9**)). The carbonyl bands, which shift to circa 1630 in ^{13}CO labelled samples, are at very low frequencies even for ketonic carbonyls, but are not without precedent; $[Pt_2Cl_2(\mu\text{-}CO)(DPM)_2]$, which has been shown to contain a ketonic carbonyl group, has the carbonyl stretch at 1638 cm^{-1}.[129] The $^{13}C\ \{^{31}P\{^{1}H\}\}$ NMR spectra of **8** and **9** consist of a doublet of doublets at circa 230 ppm as expected for a bridging carbonyl group which is coupled to two chemically inequivalent Rh nuclei (see Table 2).

The reactions of compound **1** with methyl- and phenylisothiocyanate proceed in a very different manner to those described for ethoxycarbonyl and benzoyl analogues. For these non-activated isothiocyanates no simple 1:1 adduct is observed, instead $^{31}P\{^{1}H\}$ NMR spectra of reaction solutions show a complex mixture of species at all isothiocyanate:compound **1** molar ratios. Varying the amounts of isothiocyanate does not seem to alter these spectra

significantly. On allowing the reaction mixture of compound **1** and phenylisothiocyanate to stand for several days a yellow solid (**10**) precipitates in low yield; however, the $^{31}P\{^{1}H\}$ NMR spectrum of the remaining mother liquor does not differ appreciably from that initially observed. The infrared spectrum of **10** exhibits bands at 1971 and 2165 cm^{-1}, attributable to a terminal carbonyl and isocyanide group, respectively, and this together with its elemental analysis and a comparison with the MeNC analogue (**11**) (vide infra) suggests the formulation diagrammed below. Although



R = Ph(10)
Me(11)

the trans geometry is shown, it cannot rule out that the possibility that the CO and CNMe groups are mutually cis. Both the very low solubility of **10** and its carbonyl stretch are reminiscent of the closely related species, trans-$[Rh_2Cl_2(CO)_2(DPM)_2]$ (ν(CO) = 1968 cm^{-1}).[134] In the reaction of compound **1** with MeNCS no precipitate is obtained, yet the $^{31}P\{^{1}H\}$ NMR spectrum of a fresh reaction mixture is rather similar to that observed in the PhNCS reaction. However, after several days, a complex multiplet due to a

new species (**11**) appears at δ = 20.0 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum. Although this species was not isolated, it can be identified as $[Rh_2Cl_2(CO)(CNMe)(DPM)_2]$ (**11**) based on a comparison of its $^{31}P\{^{1}H\}$ NMR and infrared (ν(CO) = 1970 cm^{-1}, ν(CN) = 2169 cm^{-1}) spectra with those of an authentic sample prepared by the 1:1 reaction of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (**1**) with MeNC.[135] It seems that both the PhNC (**10**) and the MeNC (**11**) complexes appear slowly with time, although the former is insoluble and precipitates from solution, so is not observed in the solution spectra. The analogous reactions of $[Pd_2Cl_2(DPM)_2]$ with methyl- and phenylisothiocyanate seem to proceed in a manner similar to those reported above; in these reactions the solutions are reported to contain several species from which the isocyanide complexes, $[Pd_2Cl_2(\mu\text{-}CNR)(DPM)_2]$ (R = Me, Ph), slowly precipitate in low yields.[86]

The only species which we have identified in our reactions of MeNCS and PhNCS are the final isocyanide products **10** and **11**, so no definite statement can be made regarding the mode of isocyanide production. However, two routes seem possible, either involving sulfur abstraction from one equivalent of isothiocyanate, or involving disproportionation of a condensed isothiocyanate moiety, $(SCNR)_2$. The former process for this binuclear system is favoured based on observations with other isothiocyanate

groups (vide infra) and with a related binuclear iridium system.[136] If, as is observed with the EtOC(O)NCS complex **3**, subsequent condensation of MeNCS or PhNCS ligands occurs with C-N bond formation to yield a species like that shown for species E in the scheme shown in Figure 4 (vide infra), it is difficult to envision facile isocyanide formation; in the more common condensation mode in which C-S bond formation occurs, one can readily understand isocyanide formation (vide supra). Furthermore, in some very analogous chemistry involving the binuclear iridium complex, $[Ir_2Cl_2(CO)_2(DPM)_2]$, it has been observed that reaction with one equivalent of either MeNCS or PhNCS yields stoichiometrically the sulfido-bridged isocyanide species $[Ir_2Cl_2(CO)_2(CNR)(\mu\text{-}S)(DPM)_2]$ by sulfur-carbon bond cleavage of the isothiocyanate molecule.[136] Assuming that the iridium system can serve as a model for the rhodium chemistry, it may well be that a similar process is occurring with rhodium. However, the rhodium chemistry is obviously more complex since a mixture of products is obtained in this case.

(ii) Isothiocyanate Condensation Products: Having obtained the 1:1 isothiocyanate adducts **3** and **4**, it was of interest to investigate the subsequent reactions of these species with additional isothiocyanate molecules; it seemed

that this would be a convenient way of synthesizing a variety of condensation products containing different heteroallene molecules and that such reactions could yield valuable information regarding these ligand coupling reactions. Compound **3**, the ethoxycarbonylisothiocyanate adduct, does react with a variety of isothiocyanates and CS_2 to yield a single isolable product in each case, which are shown by their elemental analyses and their conductivity and spectroscopic data to be of the form, $[Rh_2Cl_2(CO)(SCNC(O)OEt)(SCX)(DPM)_2]$ (X = NC(O)OEt (**12**), NMe (**13**), NPh (**14**), NC(O)Ph (**15**), S (**16**)). Compound **12** can also be prepared directly from **1** by reacting with two or more equivalents of EtOC(O)NCS. In no case was further reaction with these heteroallenes, to yield compounds containing more than two of these groups, observed even in the presence of large excesses of the ligand. Interestingly, the benzoylisothiocyanate adduct, **4**, does not react further with heteroallenes. The spectral parameters of compounds **12-16** are all very similar; their infrared spectra display a carbonyl stretch at <u>circa</u> 2025 cm^{-1} which shifts to <u>circa</u> 1980 cm^{-1} when ^{13}CO-substituted compound **1** is used, and all show the carbonyl stretch of the ethoxycarbonyl moiety in the region 1700-1800 cm^{-1}; in compounds **12** and **15** two organic carbonyl stretches are observed, one for each carbonyl group. These data indicate that all compounds

contain a terminal carbonyl ligand and that the organic carbonyl moieties of the ethoxycarbonylisothiocyanate group is no longer coordinated to one of the metals as suggested for compound **3** (vide supra). The $^{31}P\{^{1}H\}$ NMR spectra of compounds **12-16** are also very similar and are as expected for complexes in which the two chemically different rhodium environments render the phosphorus nuclei on each metal chemically inequivalent. Similar spectra have been successfully analyzed as AA'BB'XY spin systems, as suggested for the present compounds.[137] A typical $^{31}P\{^{1}H\}$ NMR spectrum (for compound **15**) is shown in Figure 3. Similarly, the $^{13}C\{^{31}P\{^{1}H\}\}$ NMR spectra of these species also resemble each other, displaying a doublet due to the terminal carbonyl group at circa 190 ppm with rhodium-carbon coupling of circa 70 Hz, and the ^{1}H NMR spectra show all of the required resonances which integrate according to the formulations given; for compound **12** two sets of ethyl resonances are observed showing that these groups are magnetically inequivalent.

Although the above data show that all compounds are similar and that they contain two heteroallene units they do not unambiguously establish whether condensation of these units has occurred. However, the X-ray structure determination of compound **14** does clearly establish that condensation has occurred and, based on the very close

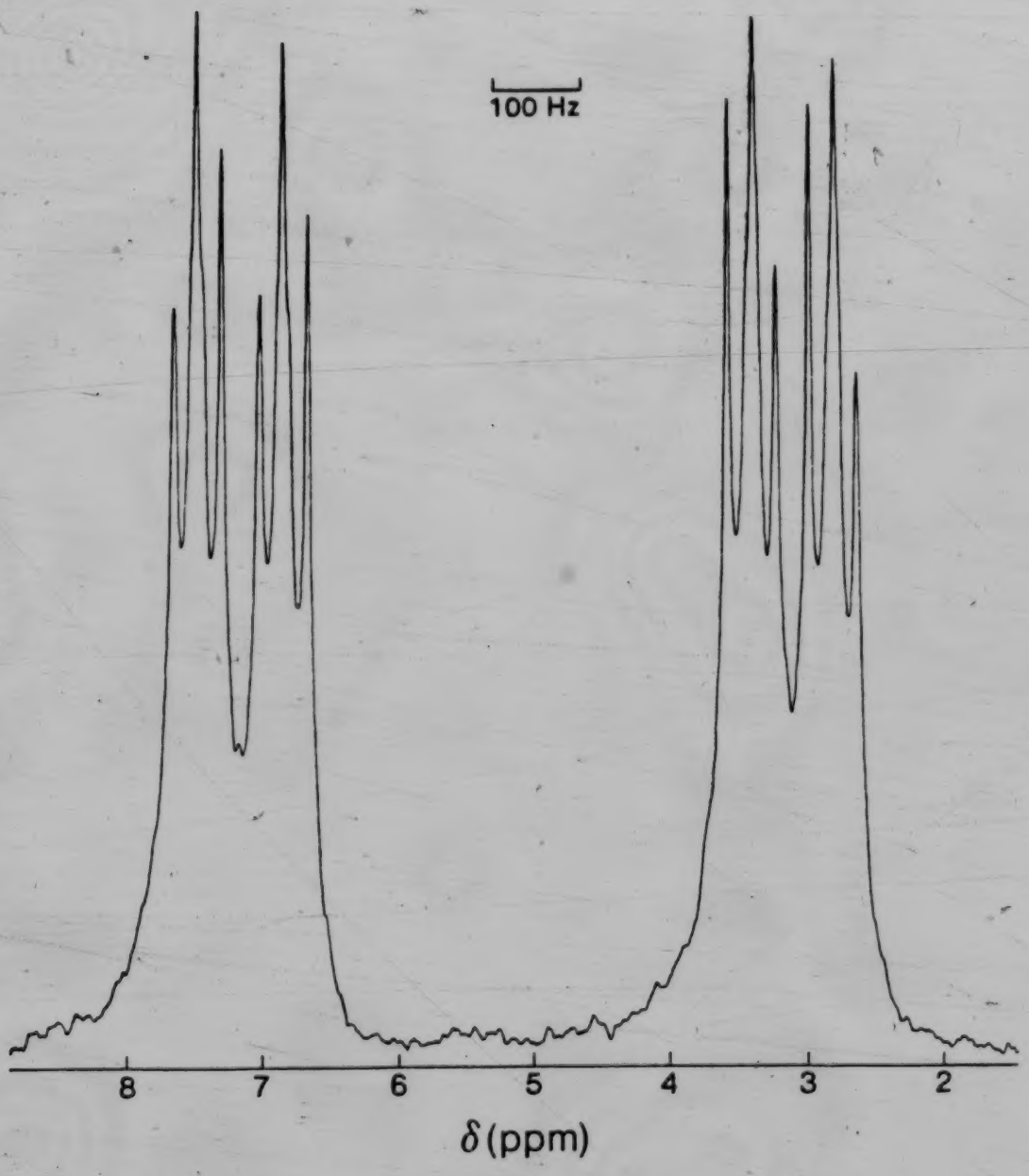
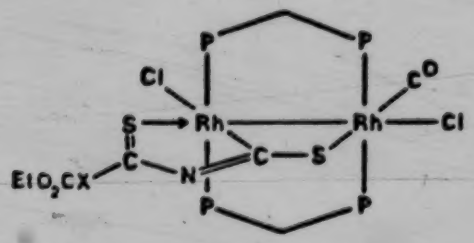


Figure 3: $^{31}P\{^{1}H\}$ NMR spectrum of $[Rh_2Cl_2(CO)\cdot(\mu\text{-SCNC(S)N(C(O)Ph)C(O)OEt)(DPM_2)]$ **(15)** obtained at 161.9 MHz.

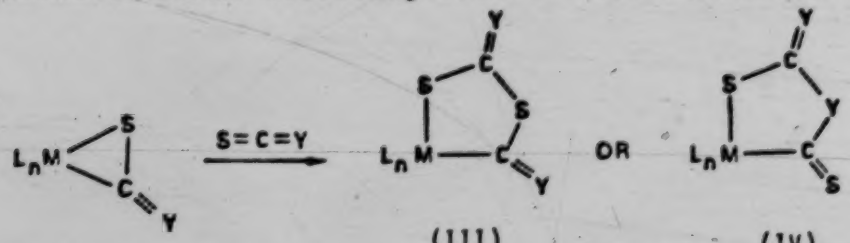
similarities between the spectral parameters for compounds **12-16**, it appears that all have the structures shown below. As noted earlier, these structures are very close to



X =	NC(O)OEt	(**12**)
	NMe	(**13**)
	NPh	(**14**)
	NC(O)Ph	(**15**)
	S	(**16**)

that reported[46,47] for the CS_2 condensation product, $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$, and again this C_2S_4 species has rather similar spectral parameters to those of compounds **12-16**. However, these compounds are not the expected products of isothiocyanate condensation reactions and are unusual in two important details; first, the condensation mode involves C-N bond formation rather than the normal C-S bond formation, and second, an ethoxycarbonyl moiety has migrated from the EtOC(O)NCS groups, which was originally coordinated in compound **3**, to the added heteroallene molecule. In sulfur-containing heteroallenes (S=C=Y) there

seems to be a marked tendency, especially with the group VIII metals, to coordinate through sulfur instead of through Y and their condensation products almost invariably result in C-S bond formation as shown for isomer III.[107] The alternate isomer resulting from C-Y bond formation (IV) has



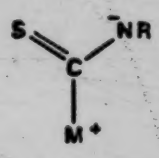
(III) (IV)

not been unambiguously established in the condensation of two heteroallene molecules although such a species has been postulated as an intermediate in the condensation of three EtOC(O)NCS molecules.[68] However, in this latter condensation of three ligands, the conventional isomer III cannot be ruled out as the first condensation product (vide infra). Nevertheless, the structure of compound **14** is the first to establish unambiguously the C-N condensation mode for isothiocyanate molecules, at least for the case involving two such molecules. It was therefore of interest to attempt to establish why C-N bond formation results for this binuclear complex whereas the related mononuclear reactions proceed so frequently by C-S bond formation.

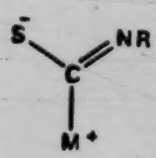
(iii) A Plausible Mechanism for Condensation and Migration. In mononuclear 1:1 isothiocyanate adducts the

isothiocyanate molecule is generally coordinated to the metal in a side-on fashion through the C-S bond.[65-72] However, it has been suggested[68] that the "active" intermediate in subsequent condensation reactions is the zwitterionic form, shown below for V, in which the ligand is η^1- bound through carbon. Based on this postulated intermediate and on the relative stabilities of the contributing resonance forms VI and VII, the tendency for

(V)



(VI)



(VII)

these species to undergo condensation reactions at sulfur rather than at nitrogen can be rationalized. Structure VI should less favourable than VII owing to the S-C π bond being weaker than that involving nitrogen and carbon, by virtue of poorer overlap between the carbon 2p and the sulfur 3p or 3d orbitals. As a consequence the sulfur atom should be more nucleophilic and should therefore be susceptible to electrophilic attack by another S=C=NR molecule with concomitant C-S bond formation. However, in binuclear systems in which the C-S moiety bridges the two metals, the binding of the second metal to sulfur significantly influences the relative tendencies of the

sulfur and nitrogen atoms to function as nucleophiles. First, the resulting four-membered M-C-S-M metallcycle in the binuclear species is less strained than the three-membered M-C-S one in mononuclear compounds, tending to favour sulfur coordination and to reduce the importance of the η^1 bonding mode in the subsequent reactivity of the former. Furthermore, coordination to the second metal in this system, it seems, lowers the nucleophilicity of sulfur owing to the formal positive charge on this atom as is suggested by a consideration of the structure of the binuclear isothiocyanate complex **14**. In this compound the short C(4)-S(1) bond suggests the importance of resonance structures H and J with the resulting charge on sulfur, as is shown at the bottom of the scheme shown in Figure 4. Although the structure of the important first product (**3**) in the condensation reactions has not been determined crystallographically, it should closely resemble that of **14**. The major difference in these structures, at least as far as the isothiocyanate ligand is concerned, should be due to replacement of the coordinated organic carbonyl group with the thiocarbonyl moiety **14** (see Figure 4). This should result in an increased importance of the structure analogous to **J** for compound **3**, owing to the more favourable C=O bond compared to C=S, and should therefore increase the nucleophilicity of nitrogen, by virtue of its formal

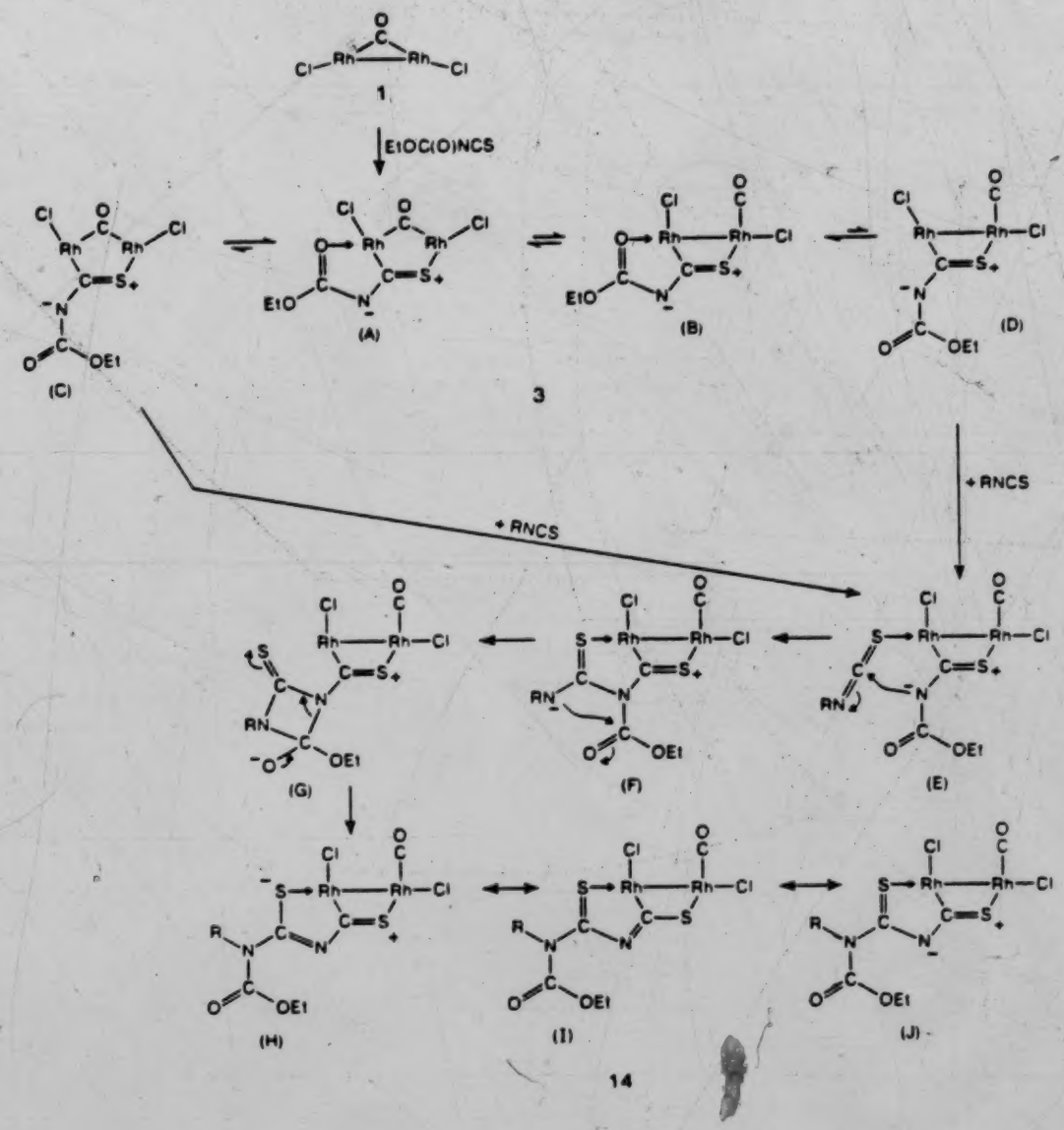


Figure 4. Scheme for the reaction of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ with activated isothiocyanates.

negative charge, leading to C-N bond formation (vide infra).

In order for condensation with other heteroallene molecules to occur, it appears that prior coordination of these groups to one of the metals is necessary; a similar conclusion was reached by Itoh and coworkers in their related mononuclear chemistry.[68] In solution, compound 3 exists as isomers **A** and **B** in the scheme, of which only **A** has a vacant coordination site. However, heteroallene coordination at this site should lead to condensation via C-S bond formation, which is not observed; it seems that the reduced nucleophilicity of S(1) does not allow this conventional condensation mode to occur. Instead, for the observed product to be obtained, condensation of the second heteroallene at the other metal center must occur. Such a vacant coordination site does result if dissociation of the coordinated ethoxycarbonyl group in **A** and **B** occurs to give **C** and **D**, respectively. The concentrations of **C** and **D** in solution must be small since no infrared stretch corresponding to the free ethoxycarbonyl group is observed. Coordination of the second heteroallene (an isothiocyanate molecule in the example shown) at this vacant site on either **C** or **D** would lead to structure **E** which then has an appropriate geometry for nucleophilic attack by nitrogen at the heteroallene carbon atom to give structure **F**. That prior coordination of the second heteroallene is

necessary is suggested by the failure of species such as allene, carbon dioxide, phenylisocyanate and methylisocyanate to react with compound **3**; these molecules would be expected to have a lower tendency to coordinate to Rh than do their sulfur-containing analogues. The next step in the scheme is the nucleophilic attack of the nitrogen of the second isothiocyanate molecule at the carbonyl carbon occurs with subsequent N-C bond formation (Structure (**G**)). The resulting four-membered 1,3 diazetidine ring will be highly strained, so it may be that in order to alleviate some of this strain the sulfur atom becomes detached from the metal as shown. Finally, by the electron reorganization shown, cleavage of the original C-N bond results in a 1,3-shift of the ethoxycarbonyl group to give the final product **14**.

The structure of compound **14**, which is also, as noted, an isothiocyanate adduct of compound **1**, can be described by a combination of the resonance structures shown for **H**, **I** and **J**. As such compound **14** also should be capable of additional isothiocyanate coordination and subsequent condensation. However, this is not the case; no further reaction of **14** is observed. The reason for this difference in the chemistry of **3** and **14** is again probably attributable to the replacement of the coordinated organic carbonyl group in the former by the thiocarbonyl moiety in the latter. In

compound **14** the most important single resonance structure is that of **H**, as evidenced by the short C(5)-N(1) and C(4)-S(1) bonds, whereas in compound **3** it appears that the structures corresponding to **A** and **B** are most important. As a result, the isothiocyanate nitrogen of compound **3** should be more nucleophilic than that of **14**, and the tendency of the latter to undergo condensation reactions should consequently be lower. But more importantly, the sulfur atom in **14** should be more tightly bound to Rh than the oxygen atom in **3** and, as a result, no vacant site is available for coordination of the additional isothiocyanate molecule, and therefore no subsequent reaction of **14** is observed.

It is interesting that the benzoylisothiocyanate adduct **4** does not undergo heteroallene condensation reactions as are observed for **3**. Both compounds **3** and **4** should be similar in their tendencies to dissociate the coordinated ethoxycarbonyl moiety generating the vacant coordination site, such as in structures C and D of Figure 4. So both species should have comparable abilities to coordinate the second heteroallene molecule. The major difference between **3** and **4** could well lie in the greater ability of the benzoyl group to delocalize electron density compared with the ethoxycarbonyl group. In compound **4** the structures analogous to **C** and **D** will have the negative charge on nitrogen effectively delocalized over the benzoyl moiety,

whereas the ethoxycarbonyl group cannot delocalize the charge extensively because the carbonyl group is strongly conjugated with the lone-pair electrons on the ethoxy group. As a result, the electron density on nitrogen and therefore its nucleophilicity is higher for the ethoxycarbonylisothiocyanate adduct than for the benzoyl analogue. This lower nucleophilicity of the latter presumably is sufficient to inhibit the condensation reaction in compound **4**. It is also possible that steric differences between the two isothiocyanate molecules play some part in the observed reactivity difference.

The scheme shown in Figure 4, which shows the addition of isothiocyanates to compound **3**, can apply equally well for CS_2 addition. Therefore, compound **3** may react with CS_2 to give $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)SC(O)OEt)(DPM)_2]$ (**16**) via an analogous mechanism as that shown.

As noted earlier, this study represents the first clear example of a condensation reaction involving two isothiocyanate molecules which proceeds by C-N bond formation. Although Itoh and coworkers postulated such an intermediate in their mononuclear chemistry,[68] based on a very careful study, it appears that the additional data given here suggest that their reactions may proceed by C-S bond formation in the first condensation step, and certainly this possibility cannot be ruled out. Thus, the first step

in the mononuclear chemistry probably involves C-S bond formation via the η^1-SCNR intermediate noted earlier. Once the sulfur end of the isothiocyanate molecule is "tied up" with the second molecule then subsequent condensation reactions must occur at nitrogen if they are to occur. In the mononuclear chemistry then, one observes condensation of benzoylisothiocyanate at sulfur to give the 2:1 product but no further reaction occurs since the nitrogen atom of the original isothiocyanate molecule is not nucleophilic enough. With the ethoxycarbonylisothiocyanate molecule, the analogous 2:1 product reacts further with C-N bond formation since the nitrogen of this ligand is sufficiently nucleophilic for condensation at this atom to occur. The difference between the binuclear chemistry described herein and the related mononuclear chemistry is that in the former a second metal center "ties up" the sulfur atom of the coordinated isothiocyanate ligand so condensation, if it is to occur, must proceed through nitrogen via C-N bond formation. Whether or not condensation at this nitrogen occurs for both the binuclear and the mononuclear chemistry depends on the nucleophilicity of this nitrogen. Thus the 1:1 binuclear isothiocyanate complexes are analogous to the 2:1 mononuclear ones of Itoh and coworkers and the 2:1 ethoxycarbonylisothiocyanate product compares with their 3:1 adduct.

Conclusions

Organic isothiocyanates are shown in the study described in this thesis to display three distinct reactivity modes with the binuclear complex $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ depending on the nature of the isothiocyanate molecule itself. The first mode observed for the so-called activated isothiocyanates EtOC(O)NCS and PhC(O)NCS, involves formation of 1:1 adducts in which the isothiocyanate ligand bridges the metal, bound by carbon to one and by sulfur to the other metal center. The ethoxycarbonylisothiocyanate adduct, in turn, reacts further with a variety of heteroallenes yielding unusual condensation products which have resulted from C-N bond formation by nucleophilic attack of the nitrogen atom of the coordinated EtOC(O)NCS ligand at carbon of the incoming heteroallene molecule. In addition, these condensation reactions are accompanied by a 1,3-shift of the ethoxycarbonyl moiety to either the nitrogen of the added isothiocyanate molecule or to one of the sulfur atoms of CS_2 if it is the added heteroallene. With the non-activated PhNCS and MeNCS molecules a third reactivity mode, yielding isocyanide ligands, is observed.

This study is significant in several aspects. It is believed to be the first in which all three types of

reaction products have been isolated and characterized for the same metal system; in particular isolation of the 1:1 ethoxycarbonylisothiocyanate adduct is an important development since it allows the preparation of a variety of heteroallene condensation products, which prove useful for delineating the reaction mechanism. This study is also the first in which the coupling of two isothiocyanate molecules by C-N, rather than by C-S, bond formation is clearly established. A scheme is presented for these two metal-center induced coupling reactions which can be applied, with slight modifications, to related mononuclear chemistry, and is therefore attractive in that it outlines a unified approach to heteroallene coupling reactions.

The presence of the second metal center in these reactions has a very significant effect on the chemistry as compared with that displayed by the mononuclear analogues. Coordination of the heteroallene sulfur atom by the second metal lowers its nucleophilicity with the result that subsequent condensation reactions occur at nitrogen rather than at sulfur. This modification of reactivity by the second metal center has obvious relevance to organic synthesis. So, for example, in this study the syntheses of a variety of new isothiocyanate molecules by the coupling of the ethoxycarbonylisothiocyanate molecule with other heteroallenes followed by the 1,3-shift of the ethoxycarbonyl group are observed.

CHAPTER THREE

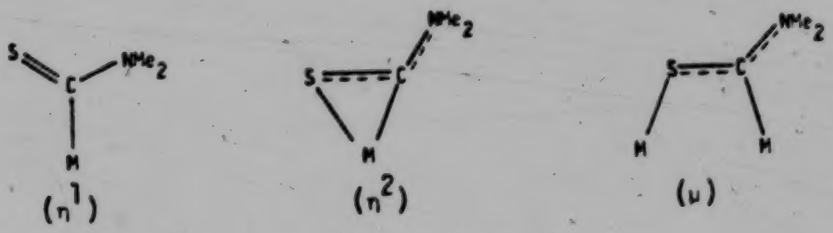
THE OXIDATIVE ADDITION OF DIMETHYLTHIOCARBAMOYL CHLORIDE TO $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2PCH_2PPh_2)_2]$.

Introduction

Metallocarboxylic acids, $L_nMC(O)OH$, also known as hydroxycarbonyls, have been proposed as key intermediates in a variety of organometallic processes, including the homogenous catalysis of the Water Gas shift reaction,[138] the reactions of metal carbonyls with water to form the related hydrides,[139,140] the isotopic exchange of metal carbonyls with water[141,142] and the oxidation of CO by metal ions.[143-145] However, only a few metallocarboxylic acid species have been isolated and characterized owing primarily to the ease with which they extrude CO_2.[146-151] In particular little is known about the bonding of the hydroxycarbonyl fragment in the presence of more than one metal centre.[152] This information is important if the function of polynuclear metal complexes in the catalysis of the above reactions is to be understood.

One approach to obtaining information about these elusive metallocarboxylic acids involves the study of model

systems in which ligands that bear similarities to the hydroxycarbonyl ligand, but which are less liable to decompose and therefore more amenable to study, are substituted for the $C(O)OH^-$ moiety. These ligands can be derived from the hydroxycarbonyl group by replacement of the carbonyl oxygen by sulfur and the OH group by an SR or NR_2 unit. The compounds so obtained obtained are quasi-isoelectronic to the related metallocarboxylic acid species, but are generally much more stable, allowing an indepth study of the chemistry of these systems to be carried out. One such model ligand for the $C(O)OH^-$ fragment that has received some attention is the dimethylthiocarboxamido group, $C(S)NMe_2^-$. This group has been found to coordinate to metals in at least three different ways. First, in the presence of a single metal center, it can be bound solely through the carbon atom, analogous to the bonding mode commonly proposed for $C(O)OH^-$,[153-155] or through the carbon-sulfur π system, forming a three membered M-C-S chelate ring.[153-173] In the presence of two metal centers, the third bonding mode, in which the carbon-sulfur bond bridges the metals, is also possible.[153-155,175-177]



Although the second[155,157,159-161,164-171] and third[175-177] bonding modes have been confirmed by single crystal X-ray diffraction studies, no such structural verification has appeared of the first.

A study of the chemistry of the $SCNMe_2^-$ group with a binuclear rhodium complex was therefore undertaken to study the possible coordination modes of this ligand in a binuclear system and in the hope that it would yield information of relevance to the related metallocarboxylic acid species. The results of this study are described in this chapter.

Experimental Details

The general experimental conditions and techniques are given in Chapter Two. Dimethylthiocarbamoyl chloride, which was recrystallized from diethyl ether prior to use, and sodium deuteroboride were purchased from Aldrich, and tetraethylammonium borohydride from Research

Organic/Inorganic Chemicals. All other reagents were, except where noted in Chapter Two, used as received. $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$[41] (**1**) and MeNC[112] were prepared by the reported procedures.

Preparation of the Complexes

(a) $[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$ (**2**). Compound **1** (100 mg, 0.093 mmol) and $SC(Cl)NMe_2$ (25 mg, 0.202 mmol) were dissolved in 10 mL CH_2Cl_2. The resulting dark brown solution was stirred at room temperature for 6 h with little solution color change. Addition of diethyl ether precipitated a brown-yellow solid, which after two recrystallizations from CH_2Cl_2/Et_2O gave **2** as a bright yellow powder. The solid was filtered in air and washed with Et_2O. Yield 20%. Spectral and conductivity details for **2** and other compounds prepared are summarized in Tables 11 and 12.

(b) $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot nCH_2Cl_2$ (**3**). Compound **1** (1.0 g, 0.932 mmol) and $SC(Cl)NMe_2$ (0.25 g, 2.2 mmol) were dissolved in 25 mL CH_2Cl_2, sufficient $NaBF_4$ to form a saturated solution (*circa* 250 mg) was added and the suspension was stirred for 4 h, by which time the color had changed from dark brown to orange-red. The solution was filtered to remove NaCl and excess $NaBF_4$, and diethyl ether

TABLE 11. Infrared Spectral and Conductivity Data.

	Compound	Infrared, cm^{-1} ν(CO)	Infrared, cm^{-1} ν(CN)	Conductivity[a], Ω^{-1} cm^2 (10^{-3} M solutions)
(2)	$[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$	1971[b] 1988, 2005(sh)[a]	1615[b]	11·9
(3)	$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$	1999[b] 2000[a]	1616[b] -	47·4
(3a)	$[Rh_2Cl_2(^{13}CO)(SCNMe_2)(DPM)_2][BF_4]$	1952[b]	1616[b]	
(4)	$[Rh_2Cl_2(SCNMe_2)(DPM)_2][BF_4]$	-	1467[b]	39·8
(5)	$[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$	-	1623, 2209(CNMe)[b]	40·6
(6a)	$[Rh_2(CO)(SCNMe_2)(THF)(DPM)_2][BF_4]$	1952[c]	-	-
(6b)	$[Rh_2(CO)(SCNMe_2)(CH_3CN)(DPM)_2][BF_4]$	1957[d]	-	-
(7)	$[Rh_2(CO)_2(SCNMe_2)(DPM)_2][BF_4]$	1988, 1948[b]	1521[b]	46·9
(7a)	$[Rh_2(^{13}CO)_2(SCNMe_2)(DPM)_2][BF_4]$	1942, 1902[b]	1521[b]	

(a) CH_2Cl_2 solution
(b) KBr disk
(c) THF solution
(d) CH_3CN solution

TABLE 12. NMR Spectral Data

No.	Compound	^1H, δ, ppm	$^{13}C\{^{31}P(^1H)\}$, δ, ppm	^1J(Rh-C), Hz	$^{31}P(^1H)$, δ, ppm	^1J(Rh-P), Hz
(2)	$[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$	2·05(s[a],3H), 2·84(s,3H)[b] 3·5(m,2H), 4·4(m,2H)[c]			4·8 (dt) 16·7 (dt)	117 91
(3)	$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$	2·05(s,3H), 2·84(s,3H)[b] 3·5(m,2H), 4·4(m,2H)[c]	186·0 (d)	81·7	4·8 (dt) 16·7 (dt)	117 91
(4)	$[Rh_2Cl_2(SCNMe_2)(DPM)_2][BF_4]$	2·10(s,6H)[b] 3·3(m,2H), 4·1(m,2H)[c]			7·1 (m) 14·9 (m) 11·5 (m)	106 104 -[e]
(5)	$[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$	2·46(s,3H), 3·01(s,3H)[b] 3·19(s,3H)[d] 3·8(m,2H), 4·1(m,2H)[c]				
(6a)	$[Rh_2(CO)(THF)(SCNMe_2)(DPM)_2][BF_4]$	(f)			14·3 (m) 24·9 (m)	157 125
(6b)	$[Rh_2(CO)(CH_3CN)(SCNMe_2)(DPM)_2][BF_4]$	1·83(s,3H), 2·65(s,3H)[b] 3·4(m,2H), 3·8(m,2H)[c]			13·6 (m) 25·2 (m)	155 123
(7)	$[Rh_2(CO)_2(SCNMe_2)(DPM)_2][BF_4]$	1·66(s,3H), 2·85(s,3H)[b] 3·3(m,2H), 3·8(m,2H)[c]	191·3 (d) 199·8 (d)	71·5 55·9	16·4 (m) 23·2 (m)	143 122

(a) Abbreviations : s, singlet, m, multiplet; dt, doublet of triplets; d, doublet

(b) Resonances due to the $SCNMe_2$ protons.

(c) Resonances due to the methylene protons of the DPM groups. These appear as an AB quartet in which each peak is further split into quintets due to virtual coupling to all P atoms.

(d) Resonance due to CNMe protons.

(e) The $^{31}P(^1H)$ NMR spectrum of 5 was recorded at 36·431 MHz only. The Rh-P coupling was not discernible at this frequency.

(f) See ref. 63.

(20 mL) added to the filtrate, precipitating a crystalline brown-red solid, which was isolated by filtering in air. The product was washed with diethyl ether, dried in vacuo, and recrystallized from CH_2Cl_2/Et_2O. Yield 1.02 g, 85%. All samples were found to contain CH_2Cl_2 of solvation, the amount of which varied depending on the exact conditions of crystallization. Analysis.[178] Calculated for $C_{54.65}H_{51.3}BCl_{3.3}F_4NOP_4Rh_2S$ (circa 0.65 CH_2Cl_2 of solvation): C, 50.3; H, 3.9; N, 1.1; S, 2.5; Cl, 8.9. Found: C, 49.2; H, 3.6; N, 1.1; S, 2.8; Cl, 8.6.

(c) $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]\cdot nCH_2Cl_2$ (**4**). Compound **3** (100 mg, 0.077 mmol) and $Me_3NO\cdot 2H_2O$ (18 mg, 0.162 mmol) were dissolved in 10 mL CH_2Cl_2. The resulting orange-red solution was stirred at room temperature for 1 h by which time the color had changed to brown. The volume of the solvent was reduced to 2 mL and 10 mL of Et_2O slowly added. Filtering the solution in air yielded a green-brown precipitate which was washed with 2-3 mL of 1:1 methanol diethyl ether to remove excess Me_3NO, and then with diethyl ether. Recrystallization from CH_2Cl_2/Et_2O gave analytically pure samples containing approximately 0.4 equivalents of CH_2Cl_2 of solvation.[178] Analysis. Calculated for $C_{53.4}H_{50.8}BCl_{2.8}F_4NP_4Rh_2S$ (n = 0.4): C, 51.12; H, 4.08; N, 1.12; Cl, 7.91. Found: C, 51.60; H, 4.20; N, 1.33; Cl, 8.04.

(d) $[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$ (**5**). A solution of **4** was prepared as described above from **3** (100 mg, 0.077 mmol and $Me_3NO{\cdot}2H_2O$ (18 mg, 0.162 mmol) in 10 mL CH_2Cl_2. Addition of 10 µL MeNC (0.17 mmol) changed the color of the solution to orange. The solution was stirred for 30 min and the volume was reduced to 2 mL. Treatment of this solution with Et_2O precipitated an orange-brown solid which was filtered from the solution in air and washed with diethyl ether. Yield 70%.

(e) $[Rh_2(CO)(Solvent)(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$.
(i) Solvent = THF (**6a**). Compound **3** (100 mg, 0.077 mmol) and $NaBH_4$ (6 mg, 0.159 mmol) were suspended in 5 mL of THF and the reaction mixture stirred at room temperature. The solids dissolved slowly over a period of about two hours yielding a deep purple, very air sensitive solution of **6a**.
(ii) Solvent = CH_3CN (**6b**). Compound **3** (100 mg, 0.077 mmol) and $Et_4N^+BH_4^-$ (22.5 mg, 0.155 mmol) were dissolved in 5 mL of CH_3CN. A vigorous reaction immediately occurred with gas evolution yielding a deep red-to-purple colored solution of **6b**. Compound **6b** was also very air sensitive so neither it nor **6a** were isolated; their spectral parameters are given in Tables 11 and 12.

(f) $[Rh_2(CO)_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (7). Method (i). A solution of compound **6a** was prepared as outlined above. The dinitrogen atmosphere in the reaction vessel was replaced with CO causing an immediate lightening of the solution color to violet. Addition of 10 mL of diethyl ether precipitated a purple microcrystalline solid **7** which was sufficiently air stable to be filtered in air. Recrystallization from CH_2Cl_2/Et_2O gave a purple product. Samples of **7** stored in air decomposed over a period of a few days to give an unidentified white solid. Samples stored under dinitrogen were stable for several weeks. The same reaction could be performed in ethanol, methanol, acetone, acetonitrile or methylene chloride (employing $Et_4N^+BH_4^-$ as the reductant in the last two solvents). Method (ii). Compound **3** (100 mg, 0.077 mmol) and $NaBH_4$ (8 mg, 0.212 mmol) were degassed in a 3-necked round bottom flask. The dinitrogen atmosphere was replaced with CO and 3 mL methanol was added. The solids dissolved and reacted to give a purple solution. Cooling to -10°C quickly precipitated a good yield of **7** as a crystalline, deep purple solid. Analysis. Calculated for $C_{55}H_{50}BF_4NO_2P_4Rh_2S$: C, 54.79; H, 4.18; N, 1.16. Found: C, 54.78; H, 4.20; N, 1.16.

Reaction of $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2]^+$ with CO.

A solution of **4** in CH_2Cl_2 was prepared as detailed above and purged with N_2. CO was briefly passed through the solution causing a color change from brown to orange-red. Comparison of the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture was that of an authentic sample of **3** indicated that **3** was the product obtained. Confirmation was obtained from a consideration of the infrared spectrum of the solid obtained by treating the solution with diethyl ether and comparing this with the spectrum of the authentic sample.

Preparation of ^{13}CO Labelled Samples.

^{13}CO labelled samples were prepared by employing ^{13}CO labelled compound **1** (for **3**) and an atmosphere of ^{13}CO for **6**.

X-ray Data Collection.

Suitable quality, amber single crystals of **3** were grown by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of the complex. Preliminary film data showed that the crystals belonged to the monoclinic system, with systematic absences characteristic of the space group $P2_1/n$ (this non-standard setting of $P2_1/c$ was retained because of a more

convenient β angle (105.95° cf. 128.8°)). Accurate cell parameters were obtained by a least-squares analysis of 12 carefully centered reflections chosen from diverse regions of reciprocal space and obtained with use of a narrow X-ray source. Data were collected on a Picker four-circle X-ray diffractometer equipped with a scintillation counter and a pulse height analyzer tuned to accept 90% of the CuKα peak. See Table 13 for pertinent crystal data and the details of data collection.

Structure Solution and Refinement.

The structure was solved in space group $P2_1/n$ by using standard Patterson, Fourier and full-matrix, least-squares techniques. All atoms, including the hydrogens, were ultimately located. Atomic scattering factors for all atoms (hydrogen[114] and others[115]) and anomalous dispersion terms[116] for Rh, Cl, S and P were taken from the usual sources. The carbon atoms of all phenyl groups were refined as rigid groups having D_{6h} symmetry, C-C distances of 1.392 Å and independent isotropic thermal parameters for each atom. The hydrogens were all input to the least-squares program as fixed contributions in their idealized positions using C-H distances of 0.95 Å and assigning them thermal parameters of 1 $Å^2$ greater than the B's (or equivalent

TABLE 13. Summary of Crystal Data and Detalis of Intensity Collection.

Cmpd	$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4].1{\cdot}B33CH_2Cl_2$
fw	1403·99
space group	$P2_{1/n}$ (non-standard setting of $P2_{1/c}$; No. 14)
a, Å	12·340(1)
b, Å	32·888(5)
c, Å	15·374(2)
β, deg	105·95(1)
V, Å^3	5999·1
ρ_{calcd}, g/cm^3	1·554 (Z = 4)
temp., °C	22
radiatn	CuKα, $\bar{\lambda}$ = 1·54178 (Ni-filtered)
detector aperture, mm	4x4
2θ limits, deg	2·0 ≤ 2θ ≤ 120·0
scan type	θ/2θ
2θ scan rate, deg/min	2·0
scan width, deg	symmetrical, [1·90 + Δ(α_1-α_2)]
bkgd	3·5° ≤ 2θ ≤ 60°, 10 sec 60° < 2θ ≤ 120°, 20 sec
rflctns measd	±h, +k, +ℓ; 9780
data used ($F^2 \geq 3\sigma(F^2)$)	4122
abs coeff μ, cm^{-1}	86·383
crystal dimens, mm	0·246 x 0·091 x 0·094
range in abs corr factors	0·369 - 0·560
final no. of parameters refined	345
error in obs of unit weight	1·855
R	0·070
R_w	0·081

isotropic B's) of their attached atom; these atoms were not refined. Absorption corrections were applied to the data by using Gaussian integration.[117]

The BF_4^- anion was found to be severely disordered; although peaks could be located in the Fourier maps which were consistent with the known geometry of this group, significant electron density was found in an essentially spherical distribution about the central peak. Attempts to fit this electron density as more than one disordered BF_4^- molecule having fractional occupancies proved unsuccessful, so only one full-occupancy BF_4^- was refined. The resulting thermal parameters of the atoms in this group are rather high and the B-F distances are less than ideal. However, this problem is not unusual for these pseudo-spherical anions and the final geometry, although distorted, clearly displays an almost tetrahedral arrangement of fluorine atoms about boron. The occupancy factors of the CH_2Cl_2 molecules were refined; that of molecule 1 (C(7), Cl(3) and Cl(4)) refined to almost 1.0 so was fixed as a full occupancy in the final cycles, whereas that of molecule 2 ultimately refined to 0.833. The thermal parameters of these solvent molecules were also large, suggesting some slight disorder of these groups. Near the end of refinement the CH_2Cl_2 and BF_4^- groups were removed, however subsequent difference Fourier maps reaffirmed their positions and showed the

smeared-out electron density associated with these groups, so they were reinserted and refined as previously.

The final model with 345 parameters refined on 4122 observations converged to R = 0.070 and R_w = 0.081; undoubtedly the badly behaved CH_2Cl_2 and BF_4^- groups hamper the final refinements. However, the complex cation is well-behaved. On a final difference Fourier map the top 20 residuals (0.9 - 0.6 e A^{-3}) were in the vicinities of the CH_2Cl_2 molecules, the BF_4^- anion and the phenyl groups. A typical carbon atom on earlier maps had an electron density of circa 2.7 e A^{-3}.

The final positional and thermal parameters for the non-group and group atoms are given in Tables 14 and 15, respectively. The idealized positional and thermal parameters for the hydrogen atoms are given in Table 16. Selected bond lengths and angles are listed in Tables 17 and 18, respectively. Least-squares planes calculations are recorded in Table 19. A listing of the calculated and observed structure amplitude factors is available.[118]

Description of Structure.

$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ (3) crystallizes with circa 1.83 molecules of CH_2Cl_2 per formula unit in the crystals studied. In other samples which were crystallized

Table 14. Atomic Positional and Thermal Parameters.

Atom	x	y	z	U11	U22	U33	U12	U13	U23
Rh1	2036 (1)	974.8 (4)	2963 (1)	324 (7)	478 (8)	366 (9)	23 (7)	71 (6)	1 (8)
Rh2	3879 (1)	1687.7 (4)	3408.0 (9)	275 (7)	380 (8)	357 (8)	12 (7)	38 (6)	8 (8)
C11	4047 (3)	928 (1)	3501 (3)	400 (23)	371 (24)	491 (28)	-5 (20)	66 (20)	4 (23)
C12	5834 (4)	1802 (2)	3925 (3)	358 (24)	800 (38)	583 (33)	-98 (23)	49 (23)	-57 (28)
C13	6165 (9)	4971 (3)	2735 (9)	1925 (105)	1673 (100)	2883 (150)	-52 (86)	986 (102)	-562 (104)
C14	3894 (8)	4738 (3)	2165 (7)	1406 (80)	1919 (102)	1675 (92)	78 (73)	119 (68)	-44 (78)
C15	8380 (12)	2120 (5)	2972 (10)	1802 (130)	2884 (201)	2103 (157)	-196 (127)	489 (110)	-960 (140)
C16	9910 (8)	2705 (4)	3864 (9)	934 (73)	1754 (116)	2199 (135)	49 (73)	-58 (77)	183 (98)
S1	2003 (4)	1962 (2)	2899 (4)	416 (27)	669 (35)	650 (36)	131 (26)	51 (24)	26 (31)
P1	2130 (3)	958 (2)	1469 (3)	322 (24)	485 (30)	440 (32)	-47 (23)	39 (23)	4 (27)
P2	3968 (4)	1639 (1)	1892 (3)	345 (24)	410 (28)	440 (31)	-30 (22)	96 (22)	23 (25)
P3	1935 (3)	985 (2)	4447 (3)	341 (24)	506 (31)	415 (31)	-73 (24)	75 (21)	-46 (27)
P4	3697 (4)	1701 (2)	4902 (3)	363 (25)	455 (30)	412 (30)	-29 (23)	72 (22)	-9 (27)
F1	7357 (15)	3422 (5)	8401 (12)	1574 (151)	1457 (160)	1172 (140)	-199 (123)	734 (118)	-327 (126)
F2	7277 (22)	3393 (7)	3775 (13)	3276 (305)	2040 (239)	1129 (161)	1199 (226)	894 (187)	298 (165)
F3	5943 (25)	3652 (7)	2771 (19)	2937 (313)	1757 (240)	2634 (307)	-304 (233)	1213 (263)	-348 (221)
F4	7504 (27)	3873 (7)	3215 (16)	4821 (467)	1536 (204)	1824 (237)	-1186 (254)	1508 (264)	-1027 (192)
O1	-386 (11)	1037 (6)	2333 (9)	521 (90)	1628 (172)	536 (102)	-15 (107)	64 (78)	-74 (108)
N1	3443 (15)	2620 (5)	3184 (11)	870 (134)	384 (106)	642 (130)	134 (97)	51 (103)	73 (91)
C1	868 (16)	1001 (7)	3589 (10)	613 (126)	881 (164)	46 (88)	-81 (120)	51 (85)	-195 (103)
C2	2229 (16)	2236 (6)	3202 (12)	827 (132)	726 (155)	359 (123)	247 (118)	145 (100)	309 (112)
C3	4619 (21)	2770 (6)	3482 (16)	1059 (197)	478 (146)	903 (201)	41 (137)	86 (158)	-165 (152)
C4	3562 (25)	2918 (7)	2931 (20)	1706 (283)	420 (154)	1517 (287)	423 (168)	366 (233)	-8 (169)
C5	2660 (13)	1426 (5)	1126 (12)	422 (100)	375 (107)	442 (119)	-43 (82)	100 (86)	-18 (88)
C6	2341 (13)	1482 (5)	4964 (12)	308 (91)	411 (104)	813 (132)	-15 (82)	169 (88)	83 (100)
C7	5246 (28)	4580 (10)	2447 (28)	1194 (277)	1191 (302)	3024 (524)	312 (234)	-350 (310)	-181 (331)
C8	8511 (47)	2525 (17)	3440 (26)	3312 (682)	2947 (624)	718 (378)	2615 (565)	645 (354)	514 (399)
B1	7256 (13)	3655 (25)	3035 (58)	2213 (306)					

*Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. The positional and thermal parameters have been multiplied by 10^4. $U_{ij}=B_{ij}/(2\,a^*_i a^*_j)$ Å^2. The thermal ellipsoid is given by $\exp(-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl))$.

TABLE 15. Derived Parameters for the Rigid Groups of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot 1\cdot 833\ CH_2Cl_2$.

Atom	x	y	z	B,Å^2	Atom	x	y	z	B,Å^2
C(11)	0.0798(7)	0.0878(3)	0.0609(7)	2.9(3)	C(51)	0.0511(9)	0.0926(5)	0.4556(9)	3.9(4)
C(12)	0.0379(10)	0.1140(3)	0.0117(9)	5.2(5)	C(52)	0.0123(13)	0.0544(4)	0.4719(11)	8.5(8)
C(13)	-0.0657(11)	0.1060(4)	-0.0735(7)	6.3(6)	C(53)	-0.0991(15)	0.0494(4)	0.4737(11)	10.4(9)
C(14)	-0.1273(8)	0.0718(4)	-0.0627(8)	4.8(5)	C(54)	-0.1717(9)	0.0826(6)	0.4592(11)	7.1(6)
C(15)	-0.0853(9)	0.4567(3)	0.0100(9)	4.6(4)	C(55)	-0.1329(12)	0.1208(5)	0.4428(11)	8.6(7)
C(16)	0.0182(10)	0.0537(3)	0.0717(7)	4.6(4)	C(56)	-0.0215(13)	0.1258(4)	0.4410(10)	6.8(6)
C(21)	0.2939(9)	0.0551(3)	0.1147(9)	3.1(3)	C(61)	0.2747(9)	0.0606(3)	0.5221(8)	3.7(4)
C(22)	0.3366(10)	0.0235(4)	0.1746(6)	4.3(4)	C(62)	0.3219(10)	0.0279(4)	0.4880(6)	4.4(4)
C(23)	0.3875(10)	-0.0098(3)	0.1460(9)	5.3(5)	C(63)	0.3813(10)	-0.0018(3)	0.5464(9)	4.1(4)
C(24)	0.3956(10)	-0.0115(3)	0.0576(10)	5.2(5)	C(64)	0.3936(10)	0.0011(4)	0.6389(8)	5.0(5)
C(25)	0.3529(11)	0.0200(4)	-0.0023(7)	6.5(6)	C(65)	0.3465(11)	0.0338(4)	0.6730(6)	6.4(6)
C(26)	0.3021(10)	0.0533(3)	0.0263(8)	4.5(4)	C(66)	0.2870(10)	0.0635(3)	0.6146(9)	4.7(4)
C(31)	0.5083(8)	0.1356(3)	0.1597(8)	3.1(3)	C(71)	0.4760(9)	0.1440(4)	0.5802(8)	3.4(4)
C(32)	0.5896(10)	0.1146(4)	0.2248(6)	3.7(4)	C(72)	0.5628(11)	0.1208(4)	0.5642(7)	4.8(4)
C(33)	0.6751(9)	0.0938(4)	0.2004(8)	5.5(5)	C(73)	0.6402(9)	0.1019(4)	0.6359(9)	7.2(6)
C(34)	0.6793(9)	0.0942(4)	0.1109(9)	5.8(5)	C(74)	0.6308(11)	0.1061(4)	0.7235(8)	5.9(5)
C(35)	0.5980(11)	0.1152(4)	0.0458(6)	5.0(5)	C(75)	0.5440(13)	0.1293(5)	0.7395(7)	6.3(5)
C(36)	0.5125(9)	0.1359(4)	0.0702(7)	4.6(4)	C(76)	0.4666(10)	0.1483(4)	0.6678(10)	5.9(5)
C(41)	0.4085(11)	0.2144(3)	0.1418(9)	3.6(4)	C(81)	0.3647(11)	0.2222(3)	0.5317(9)	3.8(4)
C(42)	0.3163(8)	0.2374(4)	0.0949(9)	5.3(5)	C(82)	0.4671(8)	0.2419(4)	0.5674(9)	5.3(5)
C(43)	0.3314(10)	0.2776(4)	0.0721(9)	7.1(6)	C(83)	0.4688(10)	0.2824(4)	0.5944(9)	6.0(5)
C(44)	0.4387(13)	0.2947(3)	0.0961(10)	6.0(6)	C(84)	0.3681(13)	0.3031(3)	0.5857(10)	7.2(6)
C(45)	0.5308(9)	0.2716(4)	0.1430(9)	6.0(5)	C(85)	0.2657(10)	0.2834(4)	0.5500(10)	6.6(6)
C(46)	0.5157(9)	0.2135(4)	0.1659(8)	4.6(4)	C(86)	0.2640(8)	0.2429(4)	0.5230(9)	5.6(5)

Rigid-Group parameters

Group	x_c[a]	y_c	z_c	Delta[b]	Epsilon	Eta
ring 1	-0.0237(7)	0.0798(3)	-0.0009(6)	3.024(9)	-2.547(8)	-0.546(9)
ring 2	0.3448(6)	0.0218(2)	0.0862(6)	0.395(17)	2.027(8)	-1.474(17)
ring 3	0.5938(6)	0.1149(2)	0.1353(6)	0.916(16)	2.070(7)	-1.515(16)
ring 4	0.4236(7)	0.2545(3)	0.1190(6)	-1.652(8)	-2.968(8)	-2.843(8)
ring 5	-0.0603(8)	0.0876(3)	0.4574(6)	0.169(10)	2.991(10)	2.842(9)
ring 6	0.3342(6)	0.0308(3)	0.5805(6)	0.339(14)	-2.112(8)	1.324(15)
ring 7	0.5534(7)	0.1251(3)	0.6519(6)	0.901(14)	-2.122(8)	1.512(13)
ring 8	0.3664(7)	0.2626(3)	0.5587(6)	1.556(8)	-3.139(9)	0.298(8)

a x_c, y_c and z_c are the fractional coordinates of the centroid of the rigid group.

b The rigid group orientation angles Delta, Epsilon and Eta (radians) have been defined previously: S.J. La Placa and J.A. Ibers, Acta Crystallogr. 1965, 18, 511.

TABLE 16. Derived Hydrogen Positions and Thermal Parameters for $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot 1.833CH_2Cl_2$.

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
H(1C3)	0·4837	0·2796	0·4136	7·6	H(35)	0·6007	0·1158	-0·0154	4·8
H(2C3)	0·5099	0·2586	0·3311	7·6	H(36)	0·4570	0·1507	0·0260	4·5
H(3C3)	0·4655	0·3031	0·3231	7·6	H(42)	0·2428	0·2259	0·0787	5·8
H(1C4)	0·2339	0·2998	0·3456	10·9	H(43)	0·2686	0·2934	0·0406	7·4
H(2C4)	0·2828	0·3147	0·2682	10·9	H(44)	0·4493	0·3221	0·0809	6·3
H(3C4)	0·1937	0·2801	0·2504	10·9	H(45)	0·6042	0·2831	0·1593	5·4
H(1C5)	0·2796	0·1382	0·0557	4·3	H(46)	0·5784	0·2156	0·1975	4·4
H(2C5)	0·2087	0·1628	0·1064	4·3	H(52)	0·0617	0·0317	0·4820	8·1
H(1C6)	0·1765	0·1671	0·4678	4·4	H(53)	-0·1257	0·0235	0·4854	9·7
H(2C6)	0·2367	0·1462	0·5586	4·4	H(54)	-0·2476	0·0795	0·4604	6·2
H(1C7)	0·5370	0·4433	0·1942	17·6	H(55)	-0·1823	0·1437	0·4322	8·4
H(2C7)	0·5349	0·4391	0·2942	17·6	H(56)	0·0051	0·1519	0·4288	7·1
H(1C8)	0·8135	0·2729	0·3026	19·6	H(62)	0·3135	0·0258	0·4248	4·1
H(2C8)	0·8213	0·2517	0·3942	19·6	H(63)	0·4134	-0·0242	0·5230	4·1
H(12)	0·0803	0·1372	-0·0195	5·5	H(64)	0·4341	-0·0192	0·6787	4·6
H(13)	-0·0936	0·1237	-0·1238	6·0	H(65)	0·3549	0·0358	0·7362	5·5
H(14)	-0·1978	0·0664	-0·1054	4·6	H(66)	0·2550	0·0858	0·6380	4·3
H(15)	-0·1281	0·0226	0·0173	4·5	H(72)	0·5695	0·1180	0·5044	4·8
H(16)	0·0458	0·0361	0·1216	4·4	H(73)	0·6994	0·0860	0·6250	6·8
H(22)	0·3310	0·0248	0·2350	3·8	H(74)	0·6835	0·0932	0·7725	5·8
H(23)	0·4163	-0·0313	0·1870	5·2	H(75)	0·5377	0·1324	0·7994	6·5
H(24)	0·4301	-0·0343	0·0382	5·1	H(76)	0·4078	0·1644	0·6788	5·6
H(25)	0·3586	0·0188	-0·0626	6·2	H(82)	0·5363	0·2279	0·5735	5·2
H(26)	0·2733	0·0749	-0·0146	4·3	H(83)	0·5388	0·2959	0·6193	6·0
H(32)	0·5867	0·1144	0·2860	3·5	H(84)	0·3692	0·3307	0·6048	7·7
H(33)	0·7304	0·0795	0·2446	5·1	H(85)	0·1971	0·2975	0·5445	6·5
H(34)	0·7374	0·0802	0·0940	5·3	H(86)	0·1946	0·2295	0·4987	5·7

TABLE 17. Selected Bond Lengths (Å) in $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot 1.833CH_2Cl_2$.

Rh(1) - P(1)	2·333(5)	P(4) - C(6)	1·848(15)
Rh(1) - P(3)	2·319(5)	P(1) - C(11)	1·823(9)
Rh(1) - Cl(1)	2·395(4)	P(1) - C(21)	1·819(12)
Rh(1) - C(1)	1·74(2)	P(2) - C(31)	1·818(12)
Rh(2) - P(2)	2·368(5)	P(2) - C(41)	1·834(12)
Rh(2) - P(4)	2·369(5)	P(3) - C(51)	1·821(13)
Rh(2) - Cl(1)	2·509(4)	P(3) - C(61)	1·823(11)
Rh(2) - Cl(2)	2·354(4)	P(7) - C(71)	1·836(11)
Rh(2) - S(1)	2·407(5)	P(4) - C(81)	1·835(11)
Rh(2) - C(2)	1·93(2)	B(1) - F(1)	1·27(7)
S(1) - C(2)	1·69(2)	B(1) - F(2)	1·42(8)
C(2) - N(1)	1·32(2)	B(1) - F(3)	1·56(7)
N(1) - C(3)	1·48(3)	B(1) - F(4)	1·10(8)
N(1) - C(4)	1·44(3)	C(7) - Cl(3)	1·69(3)
C(1) - O(1)	1·14(2)	C(7) - Cl(4)	1·69(3)
P(1) - C(5)	1·805(17)	C(8) - Cl(5)	1·50(5)
P(2) - C(5)	1·853(16)	C(8) - Cl(6)	1·77(6)
P(3) - C(6)	1·828(18)		

(ii) Non-bonding Distances (Å)

Rh(1) - Rh(2)	3·207(2)	Rh(1) - S(1)	3·249(5)

TABLE 18. Selected Angles (Deg) in $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$. 1.833 CH_2Cl_2.

(a) Bond Angles

P(1) - Rh(1) - P(3)	179.4(2)	C(3) - N(1) - C(4)	117(3)	C1(2) - Rh(2) - C1(1) - Rh(1)	179.8(2)
C(1) - Rh(1) - C1(1)	178.7(6)	Rh(1)- C1(1)- Rh(2)	81.6(1)	S(1) - Rh(2) - C1(1) - Rh(1)	0.3(2)
C(1) - Rh(1) - P(1)	90.3(5)	Rh(1)- C(1) - O(1)	177(2)	C(2) - Rh(2) - C1(1) - Rh(1)	0.2(5)
C(1) - Rh(1) - P(3)	89.5(5)	Rh(1)- P(1) - C(5)	112.7(6)	Rh(2) - S(1) - C(2) - N(1)	176.6(15)
C1(1) - Rh(1) - P(1)	90.7(2)	Rh(1)- P(3) - C(6)	111.0(6)	C(3) - N(1) - C(2) - Rh(2)	-5(2)
C1(1)- Rh(1) - P(3)	89.5(2)	Rh(2)- P(2) - C(5)	112.4(6)	C(3) - N(1) - C(2) - S(1)	-179(2)
P(2) - Rh(2) - P(4)	176.1(2)	Rh(2)- P(4) - C(6)	111.8(6)	C(4) - N(1) - C(2) - Rh(2)	177(2)
C1(1) - Rh(2) - C1(2)	94.5(2)	P(1) - C(5) - P(2)	117.4(9)	C(4) - N(1) - C(2) - S(1)	3(2)
C1(1) - Rh(2) - S(1)	116.7(2)	P(3) - C(6) - P(4)	118.0(9)		
C1(2)- Rh(2) - C(2)	104.5(6)	Rh(1) - P(1) - C(11)	116.0(4)		
S(1) - Rh(2) - C(2)	44.3(6)	Rh(1) - P(1) - C(21)	117.7(4)		
C1(1) - Rh(2) - P(2)	87.9(2)	Rh(2) - P(2) - C(31)	121.5(4)		
C1(1) - Rh(2) - P(4)	89.5(2)	Rh(2) - P(2) - C(41)	111.1(4)		
C1(2) - Rh(2) - P(2)	91.3(2)	Rh(1) - P(3) - C(51)	113.8(4)		
C1(2)- Rh(2) - P(4)	91.8(2)	Rh(1) - P(3) - C(61)	117.7(4)		
S(1) - Rh(2) - P(2)	90.3(2)	Rh(2) - P(4) - C(71)	118.9(4)		
S(1) - Rh(2) - P(4)	88.3(2)	Rh(2) - P(4) - C(81)	112.0(4)		
C(2) - Rh(2) - P(2)	91.7(6)	C1(3) - C(7) - C1(4)	112(2)		
C(2) - Rh(2) - P(4)	89.8(6)	C1(5) - C(8) - C1(6)	116(2)		
Rh(2) - S(1) - C(2)	52.9(7)	F(1) - B(1) - F(2)	105(6)		
Rh(2) - C(2) - S(1)	82.8(9)	F(1) - B(1) - F(3)	96(6)		
Rh(2) - C(2) - N(1)	145(2)	F(1) - B(1) - F(4)	133(4)		
S(1) - C(2) - N(1)	132(2)	F(2) - B(1) - F(3)	90(5)		
C(2) - N(1) - C(3)	120(2)	F(2) - B(1) - F(4)	115(7)		
C(2) - N(1) - C(4)	122(2)	F(3) - B(1) - F(4)	105(7)		

TABLE 19. Least Squares Planes Calculations.

Plane No	Equation
1	-0·0663X - 0·9978Y - 0·0027Z + 3·2927 = 0
2	0·3320X - 0·0286Y - 0·9435Z + 3·8075 = 0
3	0·3321X - 0·0600Y - 0·9413Z + 4·0071 = 0

Distances From Plane (Å)

	Rh(1)	Rh(2)	Cl(1)	Cl(2)	S(1)	P(1)	P(3)	N(1)	C(1)	C(2)	C(3)	C(4)
1	-0·0017		0·0008			0·0086	0·0088		0·0219			
2		0.0012	-0·0023	-0·0059	-0·0078					0·0015		
3					0·0005			0·0081		-0·0138	0·0025	-0·0097

under somewhat different conditions the amount of CH_2Cl_2 varied to as low as 0.4 per formula unit. One of the solvent molecules in the present structure has full occupancy and the other somewhat less (0.833). Both solvent molecules have normal geometries. There are no unusual contacts involving either the solvent molecules, the complex cation or the BF_4^- anion. The BF_4^- anion is severely disordered and as a result displays a geometry which is distorted from an idealized tetrahedron, with B-F distances ranging from 1.13(8) to 1.54(9) Å (see Table 17) and F-B-F angles ranging from 92(2)° to 130(2)° (see Table 18). Although the spread in these values is rather large, it is not unexpected considering the disorder and in spite of the distortions the mean values compare well with reported values.[179]

The complex cation is shown in Figure 5. This cation consists of two rhodium centers bridged by two mutually trans DPM groups, with the Cl, CO and $SCNMe_2$ ligands bound in the equatorial plane which is approximately perpendicular to the Rh-P vectors. As suggested by the $^{31}P\{^1H\}$ NMR spectrum (vide infra), this complex has two very different rhodium environments. Rh(1) has an essentially square planar coordination in which the two phosphines are mutually trans and the carbonyl group is trans to the bridging chloro ligand, whereas Rh(2) has a distorted octahedral geometry in

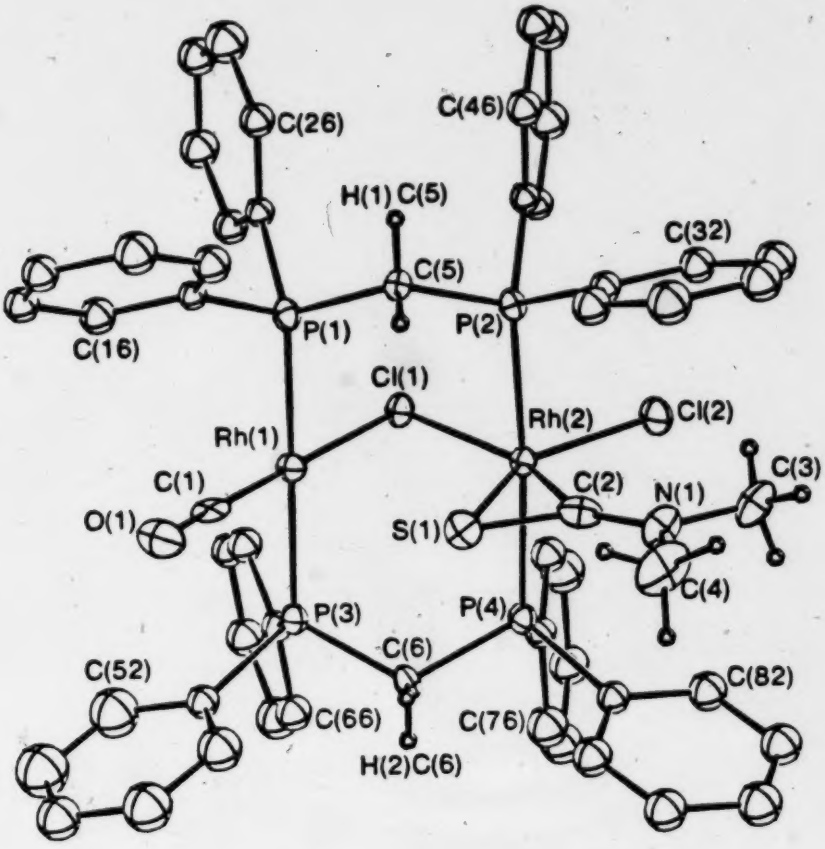


FIGURE 5. Perspective view of the $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2]^+$ cation showing the numbering scheme. The numbering of the phenyl carbons starts at the carbon atom bound to phosphorus and increases sequentially around the ring. Twenty percent thermal ellipsoids are drawn, except for hydrogen atoms which are shown artificially small.

which two of the four equatorial sites are occupied by the bridging and terminal chloro ligands and two by the side-on bound $SCNMe_2$ group. This cation represents a rare example of a binuclear rhodium species containing both 4- and 6-coordinate metal centers.[122,180] These metals can be formally regarded as Rh(I) and Rh(III) with 16 and 18 electron configurations, respectively.

Most parameters within the complex are as expected for such a DPM-bridged species and in particular those parameters involving the DPM ligands themselves are normal. As is often the case, the bridging methylene groups of the diphosphine ligands bend towards the more sterically encumbered side of the complex (that having the $SCNMe_2$ group) to allow the phenyl groups to minimize unfavourable contacts with the relatively large $SCNMe_2$ group. The Rh-P distances fall within the range normally found for these complexes, but can be grouped into two pairs; those on Rh(1) (2.319(5), 2.333(5) Å) are significantly shorter than those on Rh(2) (2.368(5), 2.369(5) Å). Presumably the longer Rh-P distances result because of the more severe steric crowding about Rh(2). A similar disparity in Rh-P distances has been observed in $[Rh_2Cl(CNMe)_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]^+$ [52] and $[Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2]$,[53] and again the larger values were associated with the more sterically encumbered Rh centers.

The chloro bridge is unsymmetrical, with the bond to Rh(1) being significantly shorter (see Figure 6). This shorter distance (Rh(1)-Cl(1) = 2.395(4) Å) is normal and compares closely with that observed in $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$,[181] in which the Cl ligand also bridges two metals which are not bonded to each other. The unusually long Rh(2)-Cl(1) distance (2.509(4) Å) can be rationalized in terms of the high trans influence of C(2) and can be contrasted with the above Rh(1)-Cl(1) distance and with the normal, terminal Rh(2)-Cl(2) distance (2.354(4) Å) on the same metal. A similar variation in metal-chlorine bond lengths has been observed in other $SCNMe_2$ complexes[155,161,164] and also in another binuclear complex containing both 4- and 6-coordinate rhodium centers.[122]

The geometry of the η^2-dimethylthiocarboxamido ligand compares well with other structurally characterized examples.[5,7,9-11,14-16,20] This group is essentially planar with the largest deviation from the least-squares plane (0.014 Å) being for C(2). Similarly, the C(3)-N(1)-C(2)-S(1) and C(4)-N(1)-C(2)-S(1) torsion angles of -179(2)° and 3(2)°, respectively, confirm the near planarity of this group. The rhodium-carbon bond length of 1.93(2) Å is intermediate between those values previously reported for $SCNMe_2$ complexes of rhodium (1.90(2), 2.00(2) Å),[161,164] and the Rh(2)-S(1) distance (2.407(5) Å),

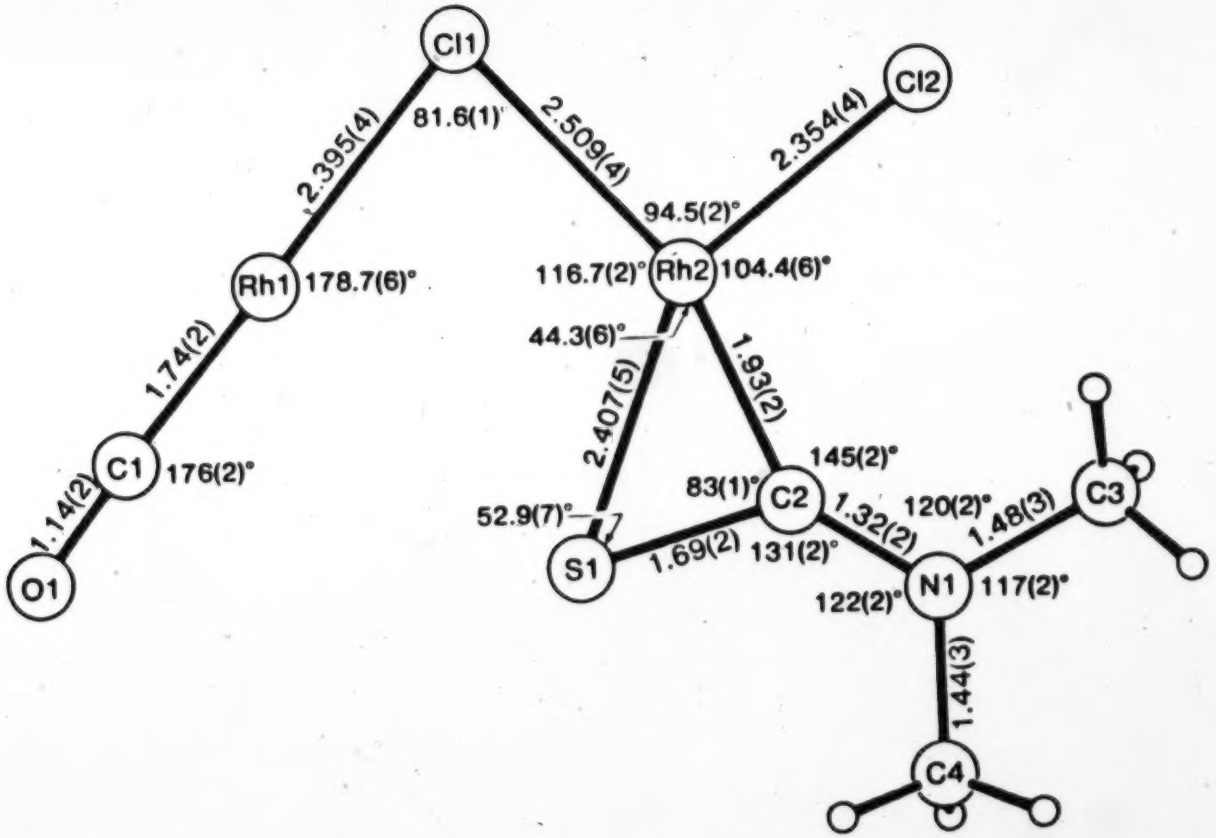
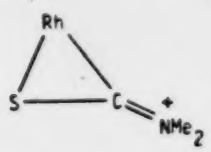
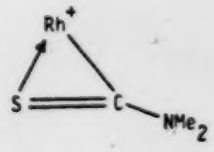


FIGURE 6. Inner coordination spheres of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2]^+$ in the approximate plane of the metals and the $SCNMe_2$ group. Some relevant bond lengths and angles are shown.

although comparable to other metal-sulfur distances for these ligands (range 2.387(2)-2.469(4) Å) is fractionally shorter than the two determinations involving rhodium (2.419(5), 2.432(5) Å).[161,164] The angle subtended by this ligand at Rh(2) (44.3(6)°) is acute but represents a normal value for such a side-on bound group.

Within the $SCNMe_2$ ligand itself, the geometry is consistent with significant partial double bond character in the S(1)-C(2) and C(2)-N(1) bonds. Thus, the S(1)-C(2) distance (1.69(2) Å) is comparable to the C-S double bond in ethylene thiourea[125] although it is longer than those in CS_2[126] and COS[127] (circa 1.55 Å). The C(2)-N(1) distance (1.32(2) Å) is typical for a C-N bond having partial double bond character and is certainly much shorter than a normal C-N single bond of about 1.47 Å.[125] Other $SCNMe_2$ complexes have displayed rather similar values (S-C range, 1.61(1)-1.69(1) Å; C-N range, 1.28(2)-1.32(3) Å). These S-C and C-N distances indicate the importance of the two tautomers, shown below, in the structure of **3**. The importance of the





first in the present structure is obvious from a consideration of the parameters around N(1); first the atoms about N(1) are planar and second C(3) and C(4) are eclipsed with respect to S(1) and Rh(2). Had the C(2)-N(1) bond been single, a pyramidal geometry about N(1) and also a twisting of the NMe_2 group about the C(2)-N(1) bond to allow these methyl groups to avoid contacts with S(1) and Cl(2) (see Figure 6) would be expected. Both the N(1)-C(3) and the N(1)-C(4) distances are normal for single bonds and are obviously significantly longer than that of C(2)-N(1), which as noted, has multiple bond character. All angles within the $SCNMe_2$ ligand are essentially as one might expect based on the above description; the angles about N(1) are all close to 120° and the S(1)-C(2)-N(1) angle (131(2)°) is comparable to the values previously reported.

Although the $SCNMe_2$ moiety is clearly bound to only one of the metal centers, it is in such a position that movement to the bridging site would require very little rearrangement; the non-bonded Rh(1)-S(1) distance is only 3.249(5) Å. The orientation of the $SCNMe_2$ group with regards to Rh(1) is clearly shown in Figure 6. This close non-bonded contact between Rh(1) and S(1) provides a rationalization for the facile interconversion of the η^2 and μ forms of this ligand (vide infra).

Discussion of Results

The majority of complexes containing the thiocarboxamido ligand ($SCNR_2$) has been prepared either by displacement of Cl^- from $SC(Cl)NMe_2$ by a metal carbonyl anion[156,158] or by oxidative addition of molecules of the type $SC(X)NMe_2$ (X = Cl[153-155,158,162,163,168] S_2CNMe_2[153,154,163] $N(Ph)SNMe_2$),[163] SMe,[163], H[177]) to a variety of metal centers. Other preparative routes, including sulfur abstraction from a dithiocarbamate ligand,[166,167,169,171] alkylation of an η^2-methyl-isothiocyanate ligand,[170] attack of an amine on a thiocarbonyl unit[172,173] and addition of SH^- to an isocyanide ligand[174] have also been used. In this work, the route involving oxidative addition of $SC(Cl)NMe_2$ to a metal substrate, namely $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$, (**1**) was utilized. This reaction in CH_2Cl_2 yields a brown solution whose $^{31}P\{^1H\}$ NMR spectrum shows the presence of only one detectable, phosphorus-containing compound (**2**). Attempts to isolate **2** give it in only low yields as a bright yellow powder. If however, $NaBF_4$ is added to the above reaction mixture a clear, red-orange solution, which has the same $^{31}P\{^1H\}$ NMR spectrum as that of **2** results (see Figure 7), from which $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2](BF_4)$ (**3**) can be isolated in high yield. The $^{31}P\{^1H\}$ NMR spectra of **2** and **3**,

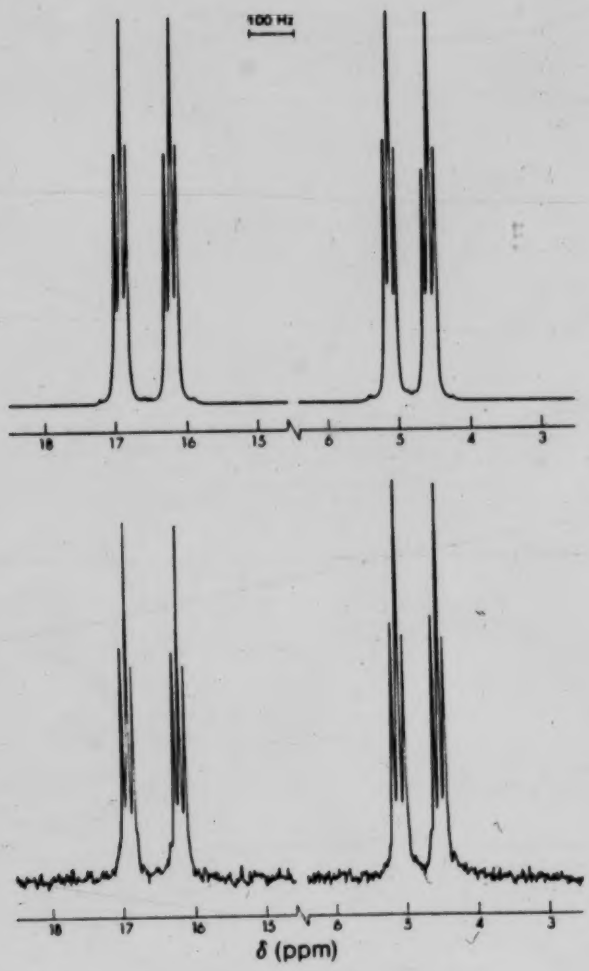
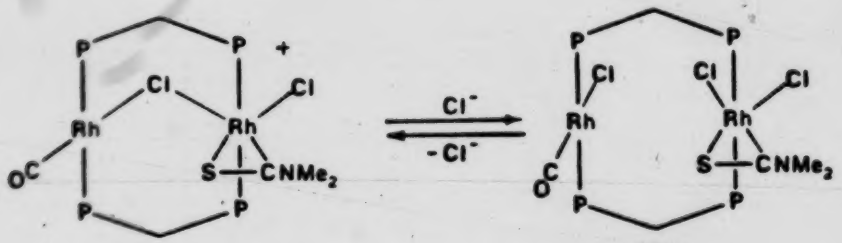


Figure 7. Simulated and experimental $^{31}P\{^{1}H\}$ NMR spectra of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2]^+$ recorded at 161.9 MHz.

shown in Figure 7, are consistent with two very different rhodium environments within the complexes, as was confirmed in the crystal structure of 3 (vide supra). A simulation of the spectrum as an AA'BB'XY system is also shown in Figure 7. The parameters used for this simulation are $\delta(P_A)$ = 4.8, $\delta(P_B)$ = 16.7 ppm, and $^1J_{Rh_X-P_A}$ = 117.6, $^1J_{Rh_Y-P_B}$ = 91.2, $^2J_{P_A-Rh_{X-P_A}}$, = 300, $^2J_{P_B-Rh_{Y-P_B}}$, = 350, $^2J_{P_A-C-P_B}$ = 23.8 and $^4J_{P-P}$ = 2.1 Hz. All other couplings were set to zero. The spectrum is rather insensitive to changes in the values of $^2J_{P-Rh-P}$ and thus these parameters were arbitrarily set at the values given. The value of $|^2J_{P-C-P} + {}^4J_{P-P}|$ can be readily obtained from the experimental spectrum, being the difference in frequency between the two smaller peaks of the 'triplet'. In fact, the positions of these bands do not change as long as $|^2J_{P-C-P} + {}^4J_{P-P}|$ is held constant; variations in the two couplings lead only to alterations in the intensity of teh sidebands with respect to the central peak. By using ^{13}CO enriched compound 1, it is possible to identify the low field ^{31}P resonance as the one due to the phosphorus nuclei on the CO-containing end of the molecule (P(1) and P(3)) since this resonance is further split into doublets with J_{P-C} = 13.5 Hz. The $^{13}C\{^{31}P\{^1H\}\}$ NMR spectrum of this ^{13}CO enriched sample consists of a doublet at δ = 186.0 ppm (J_{Rh-C} = 81.7 Hz), typical of a terminal carbonyl bound to rhodium.[22,182]

It seems that on the NMR time scale compounds **2** and **3** are essentially identical, yet there are significant differences in the two compounds. Compound **3** has a conductivity consistent with its being a 1:1 electrolyte whereas that for **2** is much less than that expected for a 1:1 electrolyte, suggesting some association of the Cl^- anion with the complex cation. In addition, their infrared spectra differ in the carbonyl region. The carbonyl stretches for **3** in the solid and in CH_2Cl_2 solution are essentially identical (1999 and 2000 cm^{-1}, respectively) suggesting the same structure in both phases. However, for **2** the solid state infrared spectrum has ν(CO) at 1971 cm^{-1} and the solution spectrum two bands - a strong one at 1988 cm^{-1} and a shoulder at 2005 cm^{-1}. These spectra suggest that in the solid state **2** has the Cl^- anion coordinated to give $[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$, as shown below. The carbonyl stretch for this species is, as expected, lower than for the cationic species **3**. In the solution infrared spectrum two species are seen which we suggest are in equilibrium; the shoulder at 2005 cm^{-1} presumably corresponds to the cationic species **3** (but with Cl^- counter ion) since the position of this band is similar to that observed with the BF_4^- anion,



(3) (2)

and the major peak at 1988 cm^{-1} appears to be due to the neutral species **2** or to something closely related to **2**. It may be that in solution **2** exists not with the Cl^- anion actually coordinated but as a close ion pair with the cationic complex; this would explain the position of the 1988 cm^{-1} band between those observed for the cationic species **3** and neutral species **2** (in the solid). Dissociation of Cl^- from **2** probably occurs because of steric crowding about Rh(2). When this occurs the chloro ligand on the other metal moves to the bridging position to give Rh(2) the 18 electron, pseudo-octahedral environment favoured for rhodium in the III oxidation state.

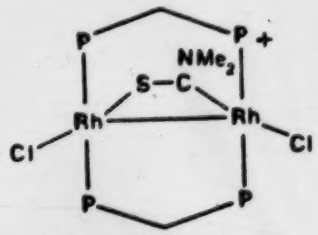
The neutral species **2**, containing Rh(I)/Rh(III) centers, is the expected product if oxidative addition occurs at one metal center. The possibility of oxidative addition at both metals to give a Rh(II)/Rh(II) system can be ruled out since the carbonyl stretch in the solid is more

consistent with a Rh(I) species (for example, it is very similar to the value of 1968 cm^{-1} observed for <u>trans</u>-$[RhCl(CO)(L_2)]_2$, $L_2 = Ph_2PCH_2PPh_2$,[41] $Ph_2AsCH_2AsPh_2$ [183]).

In the infrared spectra of **2** and **3** the C-N stretches for the $SCNMe_2$ group (1615 and 1616 cm^{-1}, respectively) are almost identical, suggesting similar bonding of these groups and both are in the region typical for a η^2-bound $SCNMe_2$ group (1570-1650 cm^{-1}).[155] Of course the X-ray structure determination unambiguously establishes this bonding mode for **3** (vide supra). The ^1H NMR spectra of **2** and **3** are also identical, showing two methyl resonances at 2.05 and 2.84 ppm, as is typically observed for an η^2-$SCNMe_2$ group.[155] The two resonances indicate that rotation about the C-N bond is restricted, probably due to the multiplicity of this bond (vide supra) and possibly also because of steric interactions with the other ligands, particularly with the phenyl groups.

It is of interest to note that the oxygen-containing analogue, $OC(Cl)NMe_2$, does not react with **1** even after refluxing in THF for several days.

Compound **3** reacts smoothly with Me_3NO resulting in carbonyl-loss, generating the A-frame species **4**. The infrared spectrum of **4** not only confirms that CO-loss has occurred but also indicates a change in the bonding



(4)

mode of the $SCNMe_2$ group; the C-N stretch of this group drops to 1467 cm^{-1}, a region typical of bridging $SCNMe_2$ groups (1460-1520 cm^{-1}).[155] In the ^1H NMR spectrum there is only one signal (integrating to 6 hydrogens) at δ = 2.10 ppm, implying rotation about the C-N bond making both methyls equivalent on the NMR time scale. This rotation is consistent with the observed drop in the C-N stretch. The $^{31}P\{^1H\}$ NMR spectrum of **4** (see Figure 8) can be simulated as an AA'BB'XY pattern, also shown in the figure. The derived parameters are $\delta(P_A)$ = 7.1, $\delta(P_B)$ = 14.9 ppm, $^1J_{Rh_X-P_A}$ = 104.2, $^1J_{Rh_Y-P_B}$ = 106.6, $^2J_{P_A-Rh_X-P_A'}$ = 300, $^2J_{P_B-Rh_Y-P_B}$ = 350, $^2J_{P-C-P}$ = 67.9 and $^4J_{P-P}$ = 15.7 Hz, with all other couplings 0 Hz. As for the spectrum of compound **3**, little effect is observed when the $^2J_{P-Rh-P}$ values are altered. The value of $|^2J_{P-C-P} + {}^4J_{P-P}|$ can be obtained easily from the experimental spectrum, being the frequency difference between the outside lines of each 5-line multiplet.

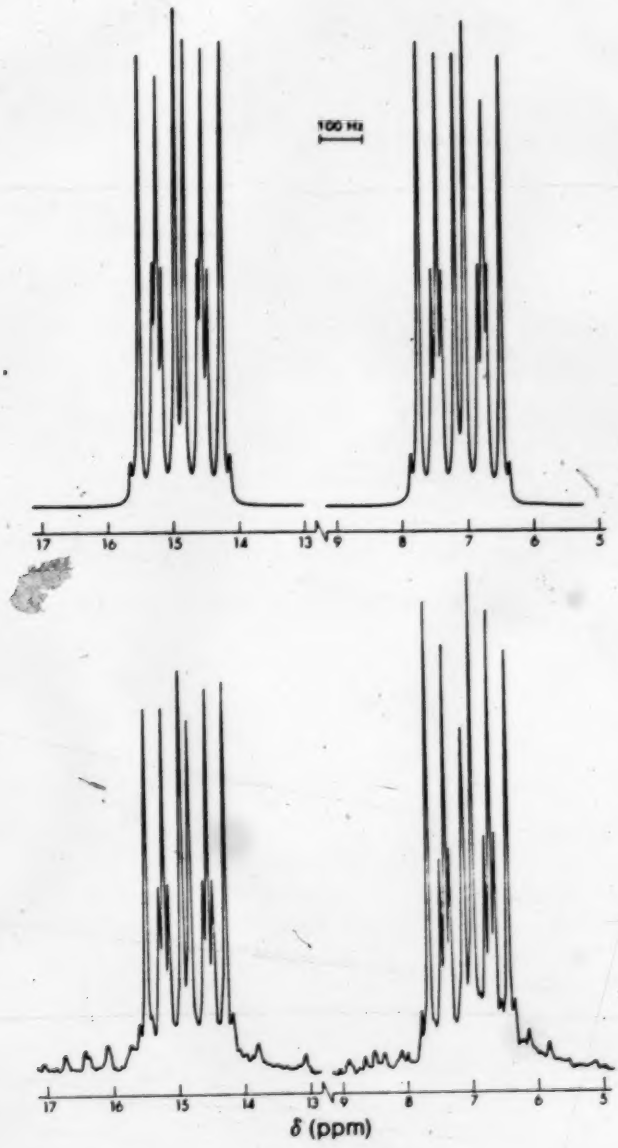
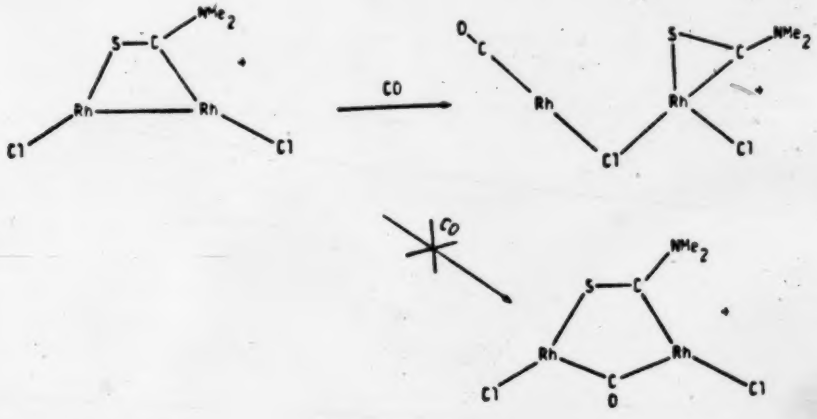


Figure 8. Simulated and experimental $^{31}P\{^{1}H\}$ NMR spectra of $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2]^+$ recorded at 161.9 MHz.

Compound **4** is structurally analogous to the acetylene-bridged species $[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$;[51] both have terminal halide ligands, a bridging group and an accompanying Rh-Rh bond. This hexafluoro-2-butyne adduct reacts with CO to yield the unusual species $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$,[52] in which CO has inserted into the Rh-Rh bond, and suggested the possibility that **4** might react likewise. However, the reaction of **4** with CO does not give the product of CO-insertion into the Rh-Rh bond, $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNMe_2)(DPM)_2]^+$, as shown below, but instead regenerates **3**, suggesting that CO attack occurs at the terminal site adjacent to the sulfur atom instead of at the bridging site. Attack at the other rhodium center to



give an isomer of **3** in which CO is adjacent to the $CNMe_2$ end of the $SCNMe_2$ ligand is presumably not favoured since the methyl groups block this coordination site. Similarly, **4**

reacts with methylisocyanide to give $[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2]^+$ (5), which is assumed to be structurally analogous to 3 but with a CNMe ligand replacing CO. The $^{31}P\{^1H\}$ and ^1H NMR spectra of 5 are similar to those of 3 (apart from the additional methyl resonance in the ^1H NMR of 5) and the infrared spectrum shows the C-N stretch of the terminal isocyanide at 2209 cm^{-1} and that of the $SCNMe_2$ group at 1623 cm^{-1}, showing that the latter group is η^2-bound to one metal center.

The facile interconversion between the chelating and bridged-bonding modes of the $SCNMe_2$ ligand, although unusual, is not surprising under the circumstances. A consideration of the structure of 3 indicates that the sulfur atom in the chelate form is only 3.249(5) Å away from the other Rh center. Upon CO-loss from 3, it takes very little movement of the $SCNMe_2$ group to give the bridging structure, which is needed to satisfy the otherwise electron deficient Rh(1). Similarly CO or CNMe attack at Rh(1) forces the $SCNMe_2$ group out of the bridging site and back to the initial η^2 mode as observed for 3.

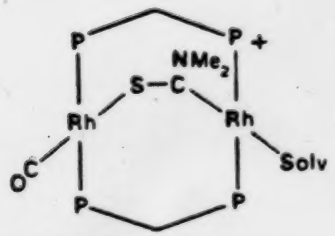
The reaction of 3 with borohydride reducing agents was undertaken in order to determine whether reduction would occur preferentially at the metal centers or at the $SCNMe_2$ ligand; examples related to both have been observed. For example, reaction of a somewhat analogous compound, trans-

$[Rh_2Cl_2(CO)_2(DPM)_2]$ with BH_4^- has been reported to yield the unusual dimer, $[Rh_2(CO)_2(DPM)_2]$, a reactive species which displays a rich chemistry with small molecules and which is a catalyst precursor for hydrogenation, hydroformylation and Water Gas Shift chemistry.[184] Although reduction of a chelating $SCNMe_2$ ligand has not been reported, reduction of the related SCSMe unit to give a thiocarbonyl ligand is a known transformation.[185] In the reaction of **3** with two equivalents of BH_4^- per dimer reduction occurs at the metals. This reaction occurs instantaneously at room temperature in a variety of solvents such as CH_2Cl_2, acetone, MeOH, EtOH and acetonitrile but more slowly in THF. However, only in the latter two solvents are single products reproducibly obtained; in all other solvents tried, reactions repeated under seemingly identical conditions give rise to either different products or to different mixtures of products. Surprisingly, no matter what solvent is used or what the products are, subsequent reaction with CO always yields the same single product (vide infra). Only the reductions in THF and acetonitrile (yielding compounds **6a** and **6b**, respectively) have been studied in detail. All reduction products are extremely air sensitive and cannot be isolated as solids. Nevertheless, the infrared and NMR spectra of the products in THF and acetonitrile solutions as well as a characterization of the subsequent product

obtained on reaction with CO allows us to propose structures for these species. The $^{31}P\{^{1}H\}$ NMR spectra of **6a** and **6b** indicate the presence of only one species in each case. These spectra are very similar to each other and also closely resemble the AA'BB'XY pattern obtained for compound **4**. Both **6a** and **6b** show a single carbonyl stretch at circa 1955 cm^{-1} in solution; unfortunately no band attributable to the C-N stretch of the $SCNMe_2$ group has been detected in either case. In most samples of **6b**[186] no hydride resonance could be detected in the ^{1}H NMR spectra, however, in some samples small amounts (< 5%) of two hydride species were observed (vide infra).[187] These NMR spectra show two resonances for the methyl groups, which, although at higher field than usually observed for complexes of $SCNMe_2$,[155] are not unreasonable. These data suggest that compounds **6a** and **6b** are not hydrides and based on the above information we propose the structures shown below. These structures are consistent with the observation that different products having a broad range in colors are obtained in the different solvents (green (EtOH, MeOH), red (acetone, CH_2Cl_2), purple (acetonitrile, THF)). Furthermore, it is consistent that for such species the solvents which have the greater coordinating ability yield products which are more stable and therefore more readily handled.

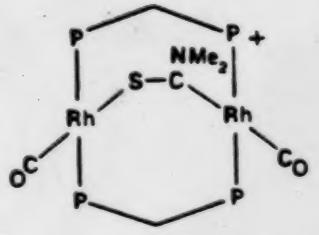
The first step in the reaction with BH_4^- is probably the formation of the dihydride, $[Rh_2H_2(CO)(SCNMe_2)(DPM)_2][BF_4]$, which then reductively eliminated H_2 to give compound **6** as the solvated species. Although two small hydride resonances were observed in the ^1H NMR spectra of some preparations of compound **6b**, it is not clear whether either of these is due to the above dihydride.

As noted earlier, the reaction of **6a**, **6b**, or any of the related reduction products in other solvents, with CO yields



(6a): Solv = THF

(6b): Solv = CH_3CN



(7)

the same single species which, based on its spectral parameters, its elemental analysis and its conductivity, has been identified as $[Rh_2(CO)_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (**7**). This species displays carbonyl stretches at 1988 and 1948 cm^{-1}, which shift to 1942 and 1902 cm^{-1} when the product is labelled with ^{13}CO, and a C-N stretch for the $SCNMe_2$ group at 1521 cm^{-1}, suggesting the bridging mode for this group

(vide supra). The infrared spectrum of **7** does not change when $NaBD_4$ is used as the reductant instead of $NaBH_4$, nor are any resonances observed in the ^1H NMR spectrum of the BH_4^- reduction product which can be attributed to a metal hydride species. The $^{31}P\{^1H\}$ NMR spectrum is qualitatively very similar to that of compound **4**, suggesting a species of similar geometry and when ^{13}CO-labelled sample is used both sets of ^{31}P resonances are split by ^{13}C, indicating that the two carbonyls are on different metals. Furthermore, the $^{13}C\{^{31}P\{^1H\}\}$ NMR spectrum, which consists of two doublets (δ = 199.8 and 191.3 ppm, $^1J_{Rh-C}$ = 55.9 and 71.5 Hz, respectively) with no ^{13}C-^{13}C coupling, confirms this conclusion. Based on these data and the conductivity, which indicates that **7** is a 1:1 electrolyte, the structure shown earlier is proposed. This structure is analogous to those of **6a** and **6b** in which CO has displaced the weakly coordinated solvent molecules. It is clear that whatever the unknown species are in the reductions of **3** in solvents other than THF and CH_3CN, their reactions with CO convert these unstable species into the air-stable dicarbonyl, **7**, probably again via displacement of the weakly coordinating solvent molecules. Unlike compound **4**, which also has a bridging $SCNMe_2$ group but which shows only one methyl resonance in the ^1H NMR, compound **7** displays two methyl resonances at 1.66 and 2.85 ppm indicating hindered rotation

about the C-N bond for the latter. This observation is consistent with the higher C-N stretching frequency observed for 7 (see text and Table 11).

Conclusions

The preparation of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ (3) by the oxidative addition of $SC(Cl)NMe_2$ to $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ in the presence of $NaBF_4$ has been accomplished. Although the $SCNMe_2$ group in compound 3 is side-on bound through sulfur and carbon to only one metal center, this groups is oriented such that the sulfur atom is close to the second metal suggesting that its interconversion between chelating and bridging coordination modes should be possible. Such facile interconversion has been observed in two reactions. First, reversible carbonyl-loss from compound 3 yields $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (4) and second, reduction of 3 by BH_4^- yields $[Rh_2(CO)(\mu\text{-}SCNMe_2)(DPM)_2(Solvent)][BF_4]$ (6); both species 4 and 6 have bridging $SCNMe_2$ groups. Another compound, $[Rh_2(CO)_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (7), also having a bridging $SCNMe_2$ moiety, can be obtained from 6 by reaction with CO.

CHAPTER FOUR

CONCLUSIONS

As stated in Chapter One, the aims of the studies described in this thesis are two-fold: to study the chemistry of sulfur containing ligands in the presence of two metal centers in order to assess the effect of the second metal, and to interpret the results in terms of their possible application to catalytic processes. The results of these studies suggest that both these objectives have, to a certain extent, been achieved.

The effect of two metal centers on the chemistry of the ligands is best observed in the reactions of the activated isothiocyanates RC(O)NCS (R = Ph, EtO) with $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$. Initial insertion of the activated isothiocyanates into the metal-metal bond of this complex occurs to give $[Rh_2Cl_2(\mu\text{-}SCNC(O)R)(DPM)_2]$, which contain the ligand in the previously unknown bridging coordination mode. The further reactions of the isothiocyanate ligand (R = EtO) with other heteroallenes to give condensation products proceed in a different manner to analogous mononuclear condensations. The reactive species in the mononuclear reactions appears to be an η^1 coordinated

isothiocyanate ligand, the sulfur atom of which possesses considerable nucleophilicity. The bridging isothiocyanate ligand does not require this type of reactive intermediate for condensation; the electronic distribution with ligand leads to the exocylic nitrogen having sufficient nucleophilicity for condensation reactions to occur. The conclusion to be drawn from this is that the reactivity of the isothiocyanate ligand is dependent on its coordination mode. The presence of a second metal therefore has importance in the transformations of this ligand.

The oxidative addition of $SC(Cl)NMe_2$ to $[Rh_2Xl_2(\mu\text{-}CO)(DPM)_2]$ occurs, in contrast, at one metal centre, with a concomitant rearrangment of some of the ligands. The crystal structure of one of these products $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ indicated, however, that the sulfur atom of the $SCNMe_2^-$ ligand is quite close to the other metal centre, suggesting that the bonding mode of the ligand could be converted to bridging. Such a conversion was achieved in a number of reactions, most notably reversibly by the removal and addition of CO.

The results of these studies can be interpreted in terms of application to catalytic processes. The altered reactivity of the isothiocyanate ligand when bridging two metals, compared to that of a chelating ligand, suggests that the reactivity of CO_2 could also depend on its

coordination mode. Thus, a CO_2 molecule coordinated to two metals in a bridging fashion may well be able to undergo transformations different to those of a terminally bound ligand.

The facile interconversion of the bonding modes of the $SCNMe_2^-$ ligand suggests that a similar process could occur for a hydroxycarbonyl ligand; both terminal and bridging coordination modes of this latter ligand are known.[152,153] The interconversion could serve to provide stability to an intermediate species, or could allow the expulsion of one fragment from the immediate environment of the ligand and the introduction of another. Such processes have been proposed[38] for many reactions (involving similar fragments) on metal surfaces.

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non-deuterated THF although both solvents were dried and degassed. Presumably small amounts of impurities in the deuterated solvent are responsible.

187. The hydride resonance, which integrate as approximately 2:1, appear as doublets of triplets: (i) δ = -16.32 ppm, $^{1}J_{Rh-H}$ = 36 Hz, $^{2}J_{P-H}$ = 10 Hz; (ii) δ = -13.72 ppm, $^{1}J_{Rh-H}$ = 28 Hz, $^{2}J_{P-H}$ = 9 Hz.